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California GAMA Domestic Wells: Nitrate and Water Isotopic Data for Tulare County

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Lawrence Livermore National Laboratory

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Final Report for the California State Water Resources Control Board

GAMA Special Studies Task 7.2 :
Specialized Analyses for GAMA Domestic Wells

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GAMA: AMBIENT GROUNDWATER MONITORING & ASSESSMENT PROGRAM SPECIAL STUDY

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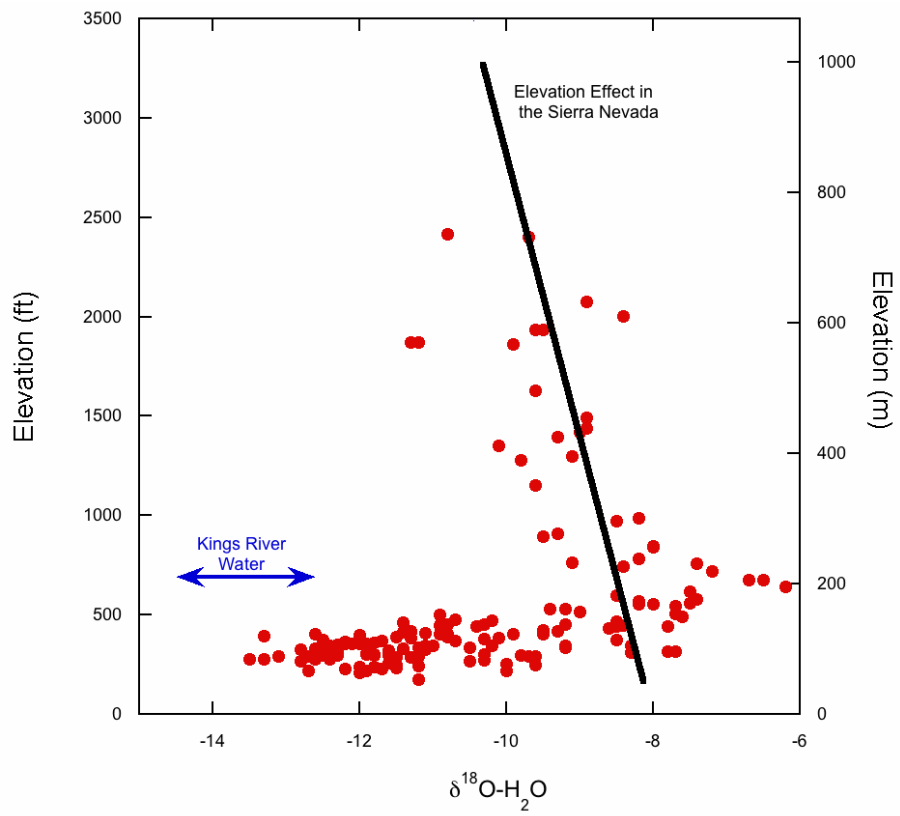

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Prepared in cooperation with the California State Water Resource Control Board

Introduction and Executive Summary

The Groundwater Ambient Monitoring and Assessment (GAMA) Program is a comprehensive groundwater quality monitoring program managed by the California State Water Resources Control Board (SWRCB). The goals of the GAMA Domestic Well Project are to provide specific information on water quality to domestic well owners, to provide a public outreach component to aid the public in understanding water quality issues affecting domestic water wells, and to help assess California groundwater quality and identify issues that may impact private domestic well water. The State Water Board works with local county agencies and Regional Water Boards to arrange sampling, which is voluntary and at no cost to the well owner. Results are shared with the well owners and used by GAMA to evaluate the quality of groundwater used by private well owners, which is largely unknown in the State of California. Lawrence Livermore National Laboratory performs specialized analyses of domestic well groundwater for the SWRCB.

In 2006, the Domestic Well Project sampled wells in Tulare County. LLNL analyzed 151 of the 181 domestic well water samples collected by the SWRCB for stable isotopes of oxygen and hydrogen in water; and analyzed 29 samples for stable isotopes of nitrogen and oxygen in dissolved nitrate. These isotopic data constrain the source of water recharging the groundwater produced by the domestic wells in this survey, and help to constrain the source of nitrate in these groundwaters.

For the purpose of discussion, wells with ground surface elevations below 400 feet are referred to as “valley” wells, and wells with ground surface elevations above 400 feet are referred to as “foothill” wells. The water isotopic evidence shows that domestic wells in the foothills (with elevations above 400 feet) receive recharge derived from local precipitation that has experienced some evaporation. In contrast, valley domestic wells below 400 feet surface elevation draw on groundwater heavily impacted by irrigation with Kings and Kaweah River water, as indicated by water isotopic composition. This finding is consistent with both the long and heavy usage of Kings River water for irrigation in this area, and with the assumed shallow depth of these domestic wells. Nitrate associated with these waters is presumably associated with the same source (chemical or organic fertilizer in irrigation water) or is mobilized by irrigation (septic effluent or soil nitrogen compounds).

Foothill and valley domestic wells in Tulare County differ in dissolved nitrate concentration (SWRCB, 2010). In general, foothill wells have low nitrate concentrations, while valley wells have moderate to high nitrate concentrations. Nitrate concentrations in the most polluted wells are sufficiently high to preclude a significant contribution from soil or atmospheric sources. Such

sources cannot be precluded in wells with nitrate concentrations below the regulatory drinking water limit, however the data set does not include enough samples near typical background concentration levels to assess the isotopic characteristics of natural nitrate sources in this area.

Nitrate isotopic compositions indicate a dairy manure or septic effluent source for the majority of the most heavily impacted wells, with the exception of one well with high nitrate concentration and an isotopic composition indicative of a synthetic fertilizer source. For less heavily impacted wells, the sparse nitrate isotopic data alone does not definitively constrain the nitrate source. The observed pattern could be produced by a single source (natural soil N) or by mixing between multiple sources (fertilizer, manure, septic). An analysis of land use and the distribution of potential nitrate sources would be extremely useful.

A preliminary investigation of the correlation between land use and nitrate isotopic composition was conducted (see Appendix "GAMA Domestic Well Project - Tulare County. Nitrate Source Attribution: The Isotopic Evidence"). The sparse nitrate isotopic data set, and the cursory approach to assigning land use limit conclusions, but patterns observed are suggestive of multiple anthropogenic sources, including dairy wastewater, septic effluent and synthetic fertilizer.

Significant findings of the study are listed below:

- Nitrate isotopic composition appears to vary with land use
  - Dairy, agricultural/residential, and wild-land sites are isotopically distinct
  - Dairy site nitrate-N isotopic data are isotopically consistent with a manure source
  - Nitrate-O isotopic data are isotopically consistent with local nitrification of ammonium (from manure, septic effluent, or synthetic ammonium fertilizer)
- The isotopic evidence is consistent with more than one nitrate source
  - Domestic wells located close to dairies frequently have a different nitrate isotopic composition than wells not close to dairies in similar hydrogeologic settings.
  - The isotopic compositions measured are consistent with the suspected sources of nitrate to these wells (soil, fertilizer, manure, septic or community wastewater).
  - High concentrations of nitrate occur in all developed land use categories.

Sampling Protocols and Analytical Methods

SAMPLE HANDLING

Sampling and handling requirements, including hold times, are listed in Table 1. Groundwater samples for the project were collected by State Water Resources Control Board. Samples for specialized analyses were collected following guidance provided by LLNL. When possible, wells were purged by pumping at least three (3) well casing volumes were pumped prior to collecting the water sample. Samples collected for determination of nitrate and water stable isotope composition do not require filtering.

Stable isotopes of water: A 30-mL glass bottle (clear, French-square type) with Qorpak™ polyseal-lined cap is triple rinsed with water directly from the sampling port, then filled just below the threads on the bottle. Filtering, preservatives and/or refrigeration are not required, but the cap should be tightly closed. Samples may be shipped at room temperature or in a cooler with ice, and are stored at room temperature.

Stable isotopes of nitrate: Either a 50-mL polyethylene centrifuge tube or a small (60-mL or 125-mL) HDPE bottle is triple rinsed with water directly from the sampling port, then filled with approximately 40-mL of sample water leaving sufficient head space to accommodate freezing.

Shipping and preservation: During field sampling, samples were shipped to LLNL by next-day service within three days of collection. Upon arrival at LLNL, samples were logged with both the supplied GAMA Domestic Wells Project ID and with a unique LLNL ID and preserved appropriately. Water Board staff also supplied LLNL with nitrate concentration data for collected samples to allow appropriate aliquoting for nitrate isotopic composition analysis. For samples collected for nitrate isotopic composition determination, a small aliquot was taken for confirmation of nitrate concentration by ion chromatography as necessary and the remainder of the sample was frozen. Samples collected for determination of water isotopic composition were stored at room temperature with a tightly sealed cap.

Table 1: Sampling and Handling Requirements for Stable Isotope Analysis

Determination	Container	Min. sample size (mL)	Preservation	Recommended Hold	Regulatory hold
Nitrate $\delta^{18}O$ and $\delta^{15}N$	Plastic	30 mL	Refrigerate at 6°C or freeze	6 months after thawing	Not applicable
Water $\delta^{18}O$ and $\delta^{2}H$	Glass	30 mL	None	1 year	Not applicable

STABLE ISOTOPE TERMINOLOGY AND REPORTING

Isotopic composition is determined by measuring the atom ratio of a minor abundance isotope to a major abundance isotope. For oxygen, the ratio measured is $^{18}O/^{16}O$, i.e. the atom ratio of Oxygen-18 to Oxygen-16. Oxygen-18 is a minor isotope of oxygen (approximately 0.2% of oxygen isotopes are ^{18}O), while Oxygen-16 is the major isotope of oxygen (approximately 99.76% of oxygen isotopes are ^{16}O).

For hydrogen, the ratio measured is $^{2}H/^{1}H$, i.e. the atom ratio of hydrogen-2 (~0.015%, abundant) to hydrogen-1 (~99.985% abundant). Hydrogen-2 is also referred to as deuterium. For nitrogen, the ratio measured is $^{15}N/^{14}N$, i.e. the atom ratio of nitrogen-15 (~0.37% abundant) to nitrogen-14 (~99.63% abundant).

Isotope ratios are reported in the standard delta (δ) notation as parts per thousand (per mil or ‰) variations relative to a reference material of known composition and defined by the following equation:

$$\delta_x = 1000 \frac{R_x - R_{ref}}{R_{ref}}$$

where R_x is the ratio of the sample and R_{ref} is the ratio of the reference material. For oxygen and for hydrogen in water, we use Vienna Standard Mean Ocean Water (VSMOW; Craig, 1961). We also use VSMOW for oxygen in nitrate. For nitrogen in nitrate, we use air as a reference material.

ANALYTICAL METHODS—STABLE ISOTOPES OF WATER

Water $\delta^{18}O$ and $\delta^{2}H$ values are determined on unfiltered samples. Water $\delta^{2}H$ is determined on unfiltered samples, usually the same bottle collected for water-$\delta^{18}O$. Oxygen isotope analyses are conducted using the carbon dioxide equilibration method for $^{18}O/^{16}O$ and analyzed with an automated water equilibration unit. Hydrogen isotope compositions of water were analyzed using the Pt-H_2 equilibration method. Isotope ratio measurements are performed on a VG PRISM III isotope ratio mass spectrometer housed in the Chemical Sciences Division at Lawrence Livermore National Laboratory. The LLNL standard operating procedure for determination of the stable isotopic composition of water in groundwater samples is SOP-UGTA-128, and is available upon request.

Analyses in the Stable Isotope Laboratory are calibrated to internal standards referenced against National Institute of Standards and Technology (NIST) standard reference materials. The waters chosen as in-house standards consist of three isotopically distinct water samples (δ18O = -3.1, -9.9 and -15.5‰). The composition and isotopic values of these internal standards span the range of natural waters typically observed in potable groundwater of California. For each set of $\delta^{18}O$ analyses, 2 each of 3 internal standards are also analyzed and used for calibration. The internal standards are periodically compared to the three NIST reference standards (NIST RM 8535; NIST RM 8536; NIST RM 8537): SMOW, Standard Light Antarctic Precipitation (SLAP), and Greenland Ice Sheet Precipitation (GISP). The analytical precision for these $\delta^{18}O$ measurements, from one run to the next, is ± 0.10‰, and the analytical precision for $\delta^{2}H$ values is ± 2‰.

Craig, H., 1961. Standard for reporting concentrations of deuterium and oxygen-18 in natural waters. *Science* **133**, 1833-1834.

Epstein, S.; Mayeda, T. K., 1953**,**Variation of O-18 content of waters from natural sources. *Geochim. Cosmochim. Acta,* **4**, 213-224.

Coplen, T. B., Wildman, J. D., and Chen, J., 1991, Improvements in the gaseous hydrogen-water equilibration technique for hydrogen isotope-ratio analysis: *Analytical Chemistry*, **63**, p. 910-912.

ANALYTICAL METHOD—STABLE ISOTOPES OF NITRATE

The isotopic composition of dissolved nitrate ($\delta^{15}N$ and $\delta^{18}O$) is determined on water samples filtered through 0.2 µm syringe filters (0.45 µm filters may be used for pre-filtering sediment-laden water). The samples are stored frozen in pre-cleaned, HDPE bottles. Samples are analyzed using an automated version of a new microbial denitrifier method (Casciotti et al., 2002; Sigman et al., 2001). In this method, a strain of denitrifying bacteria is used to reduce dissolved nitrate in water samples to N_2O gas that can be analyzed for N and O isotopic composition on the MicroMass IsoPrime IRMS. Dr. Mike Singleton, the Stable Isotope Mass Spectrometry Laboratory Manager, has implemented this method at the Center for Isotope Geochemistry at Lawrence Berkeley National Laboratory (LBNL) and in the Chemical Sciences Division at LLNL. He has safely carried out carried out hundreds of successful analyses over a period of four years. The original method has been adapted to decrease the time required for culture preparation and sample processing.

Casciotti, K. L.; Sigman, D. M.; Hastings, M. G.; Bohlke, J. K.; Hilkert, A., Measurement of the oxygen isotopic composition of nitrate in seawater and freshwater using the denitrifier method. *Analytical Chemistry* **2002,** *74*, 4905-4912.

Sigman, D. M.; Casciotti, K. L.; Andreani, M.; Barford, C.; Galanter, M.; Bohlke, J. K., A bacterial method for the nitrogen isotopic analysis of nitrate in seawater and freshwater. *Analytical Chemistry* **2001,** *73*, 4145-4153.

Singleton, M.J., K.N. Woods, M.E. Conrad, D.J. DePaolo and P.E. Dresel. Tracking sources of unsaturated zone and groundwater nitrate contamination using nitrogen and oxygen stable isotopes at the Hanford Site, Washington. *Environmental Science and Technology,* **2005**, *39*(10), 3563 – 3570.

DATA QUALITY OBJECTIVES AND QUALITY CONTROL

Data Objectives: Minimum acceptable measurement quality objectives (MQOs) for analytical techniques used in this project are summarized in Table 2. The MQOs for isotopic analyses reflect "accepted methods" for publication in high-quality scientific journals. Whenever possible, the methods with greater sensitivity and lowest detection limit will be employed as the primary method. Methods with lesser sensitivity and higher detection limits will be used for samples

known to contain high concentrations of analytes, field confirmations, or as back-up methods in the case that the primary methods are not available or functioning properly for a particular sampling event. Analyses that do not meet minimum acceptable data quality objectives will be re-run when sample is available. When sample is not available, such data will not be reported or will be reported and flagged.

Precision and Accuracy: Precision (e.g., the reproducibility among replicate samples) will be determined by analysis of duplicate samples, laboratory control standards and matrix spikes as appropriate for each method. Precision is determined as the standard deviation of measurements divided by the mean and multiplied by 100. Precision measurements will be determined on both field and laboratory replicates).

Accuracy (e.g., how close the measurement is to the true value) will be measured on one or more quality control check standards (QCCS) prepared exactly as the calibration standards. The QCCS is analyzed after the calibration standards. The QCCS should be within 10 % of the actual concentration or problems will be resolved and samples re-analyzed. For some methods, accuracy cannot be rigorously determined because there are no absolute external standards available.

Quality Control: Quality control samples will be analyzed to ensure valid data are collected. Field duplicates are collected and analyzed for at least every 20th sample. The precision of duplicates and splits are used to help identify sampling handling and preparation problems. All samples that fall outside the expected range for the sample type, location, and collection time are assessed for proper size and instrument function. The expected ranges are dependent on many factors and cannot easily be defined. Expected ranges are therefore determined on a case by case basis, initially by the analyst and finally by the PI in charge of data interpretation. Samples are re-analyzed as necessary to achieve the desired precision.

Instrument behavior is assessed by analysis of working standards as described in the individual SOPs for the various analysis types. Instruments are regularly tested for stability and linearity as described in Section 15 below. LLNL laboratories routinely participate in international calibration exercises to ensure the precision and accuracy of data reported. All instruments are regularly calibrated using NIST or IAEA standard reference materials with internationally-agreed-upon values. When in-run reference standards do not meet precision or accuracy criteria, samples from the same run will be re-analyzed. Records of instrument performance will be maintained indefinitely. All laboratories use Good Laboratory Practices (GLP), and routine analyses follow SOPs.

Table 2: Data Quality Objectives and Reporting for Stable Isotope Analysis.

Parameter	Method/ Range	Units	Reference	External Precision[1]	Instrumental precision[2]
Nitrate $\delta^{18}O$ **Nitrate $\delta^{15}N$**	Continuous Flow Mass Spectrometry	Per mil (‰)	$\delta^{15}N$: Air $\delta^{18}O$: VSMOW	$\delta^{15}N$ ± 0.3 ‰ $\delta^{18}O$ ± 0.8 ‰	$\delta^{15}N$ ± 0.2 ‰ $\delta^{18}O$ ± 0.5 ‰
Water $\delta^{18}O$ **Water $\delta^{2}H$**	Dual Inlet and/or Continuous Flow Mass Spectrometry	Per mil (‰)	$\delta^{18}O$: VSMOW $\delta^{2}H$: VSMOW	$\delta^{18}O$ ± 0.3 ‰ $\delta^{2}H$ ± 2 ‰	± 0.15 ‰ ± 1 ‰

1. External (1 sigma) precision objectives apply to replicate analyses of a single sample.
2. Instrumental precision (1 sigma) applies to calibration check samples, laboratory control samples and other measurements of samples of known concentration and isotopic composition where the known value is compared to the measured value.
3. VSMOW = Vienna Standard Mean Ocean Water

Data: Tulare County Domestic Wells

SAMPLE ISOTOPIC DATA

This data report represents specialized analyses performed by LLNL on domestic well groundwater samples collected in Tulare County by State Water Resources Control Board staff for the GAMA Domestic Wells Project. Samples were collected between April, May and June of 2006. In total, LLNL analyzed 151 samples for water isotopic composition of both oxygen and hydrogen, and 29 samples for nitrate isotopic composition of both nitrogen and oxygen. Analyzed samples included 15 field duplicates for water isotopic composition; and two field duplicates for nitrate isotopic composition. Data are tabulated in Table 3. Sample name are of the form “TUL nnnn”. Samples with nnnn less than 1000 are labeled to as either “TUL nnn” or “TUL 0nnn” or TULnnnn. These two forms are equivalent, e.g. TUL 979, TUL 0979, and TUL0979 all refer to the same sample.

Table 3: Water and Nitrate Isotopic Composition in Tulare County Domestic Well Water Samples

SWRCB ID	LLNL ID	Collection Date	Water-$\delta^{18}O$ (‰, VSMOW)	Water-$\delta^{2}H$ (‰, VSMOW)	Nitrate-$\delta^{15}N$ (‰, Air)	Nitrate-$\delta^{18}O$ (‰, VSMOW)
TUL 901	103893		-12.4	-89		
TUL 902	103894		-12.8	-93		
TUL 903	103895		-12.5	-89		
TUL 904	103896	04/18/2006	-10.2	-74		
TUL 905	103897	04/18/2006	-12.2	-87		
TUL 906	103898		-12.2	-87		
TUL 907	103899	04/18/2006	-10.8	-81		
TUL 908	103900	04/18/2006	-12.5	-89		
TUL 909	103904	04/19/2006	-12.0	-84		
TUL 910	103905	04/19/2006	-10.8	-79		
TUL 911	103906	04/19/2006	-11.3	-81		
TUL 912	103907	04/19/2006	-10.9	-82		
TUL 913	103908	04/19/2006	-11.4	-81	0.0	3.7
TUL 914	103909	04/19/2006	-10.9	-80		
TUL 915	103910	04/19/2006	-8.0	-59		
TUL 916	103911	04/19/2006	-7.7	-58		
TUL 917	103912	04/19/2006	-10.8	-80	7.7	-1.7
TUL 918	103915	04/20/2006	-9.6	-67		
TUL 919	103913	04/19/2006	-7.5	-58		
TUL 920	103916	04/20/2006	-8.9	-65	1.5	2.8
TUL 921	103917	04/20/2006	-8.2	-58		
TUL 922	103918	04/20/2006	-9.9	-74		
TUL 923	103919	04/20/2006	-9.2	-63		
TUL 924	103920	04/20/2006	-9.4	-71	5.6	1.8
TUL 925	103921	04/20/2006	-11.3	-83		
TUL 926	103922	04/20/2006	-12.4	-87		
TUL 927	103923	04/20/2006	-11.2	-79		
TUL 928	103924	04/20/2006	-8.3	-64	6.2	11.0
TUL 929	103901		-11.9	-86		
TUL 930	103954	04/25/2006	-11.3	-82		
TUL 932	103956	04/25/2006	-10.1	-76	3.5	-4.3
TUL 933	103957	04/25/2006	-10.7	-80		
TUL 934	103958	04/25/2006	-7.7	-64		
TUL 935	103976	04/27/2006	-9.2	-71	6.6	3.8
TUL 936	103966	04/26/2006	-11.8	-86		
TUL 937	103967	04/26/2006	-12.7	-91		
TUL 938	103968	04/26/2006			4.8	-3.2
TUL 939	103969	04/26/2006	-12.8	-92		
TUL 941	103960	04/25/2006	-12.4	-86	8.2	-0.3
TUL 943	103962		-11.2	-79		
TUL 944	103980	04/27/2006	-10.4	-74	8.6	1.3
TUL 945	103977	04/27/2006	-7.8	-63		
TUL 946	103978	04/27/2006	-11.1	-77		
TUL 947	103963		-12.0	-84		
TUL 948	103970	04/27/2006				

SWRCB ID	LLNL ID	Collection Date	Water-$\delta^{18}O$ (‰, VSMOW)	Water-$\delta^{2}H$ (‰, VSMOW)	Nitrate-$\delta^{15}N$ (‰, Air)	Nitrate-$\delta^{18}O$ (‰, VSMOW)
TUL 949	103971	04/26/2006				
TUL 950	103972	04/26/2006			8.0	1.8
TUL 951	103973	04/26/2006				
TUL 952	103974	04/26/2006				
TUL 954	103964	04/26/2006	-12.4	-88	8.1	-0.8
TUL 955	103965	04/26/2006	-7.8	-63		
TUL 956	103975	04/25/2006				
TUL 957	103979	05/09/2006	-7.8	-63		
TUL 978	104106	06/06/2006	-8.5	-62	6.4	3.1
TUL 979	104107	06/06/2006	-7.8	-60	6.1	8.2
TUL 980	104108	06/06/2006	-9.1	-63	3.3	3.8
TUL 981	104025	05/16/2006	-6.5	-55		
TUL 981-1	104027	05/16/2006	-6.7	-55		
TUL 982	104026	05/16/2006	-8.5	-62		
TUL 983	104028	05/17/2006	-11.5	-85	7.2	3.8
TUL 984	104029	05/17/2006	-9.3	-66		
TUL 985	104030	05/16/2006	-9.6	-66		
TUL 986	104031	05/18/2006	-10.3	-72		
TUL 987	104032	05/18/2006	-9.6	-66		
TUL 988	104109	06/06/2006	-8.3	-62	7.2	1.8
TUL 989	104116	06/07/2006	-10.1	-74		
TUL 990	104033	05/16/2006	-7.4	-59		
TUL 991	104034	05/16/2006	-9.2	-71		
TUL 992	104035	05/18/2006	-11.5	-81		
TUL 993	104036	05/17/2006	-13.3	-98		
TUL 994	104037	05/17/2006	-9.5	-70		
TUL 995	104038	05/17/2006	-7.4	-54		
TUL 996	104039	05/16/2006	-11.8	-83		
TUL 997	104040	05/17/2006	-9.3	-71	7.0	3.3
TUL 998	104041	05/17/2006	-7.2	-60		
TUL 999	104042	05/18/2006	-11.2	-79		
TUL 1000	104043	05/18/2006	-12.0	-87		
TUL 1001	104044	05/16/2006	-10.8	-74		
TUL 1002	104045	05/16/2006	-8.9	-65		
TUL 1003	104046	05/18/2006	-12.3	-88		
TUL 1004	104047	05/18/2006	-11.5	-82		
TUL 1005	104110		-10.7	-76	2.9	-0.3
TUL 1006	104117	06/08/2006	-10.3	-74	5.1	0.3
TUL 1007	104118	06/07/2006	-12.7	-94	5.3	-0.2
TUL 1008	104119	06/08/2006	-9.5	-73		
TUL 1009	104120	06/07/2006	-8.0	-59		
TUL 1010	104066	05/24/2006	-13.3	-97		
TUL 1011	104067	05/24/2006	-10.0	-70		
TUL 1012	104068	05/24/2006	-10.3	-72		
TUL 1013	104069	05/24/2006	-11.6	-84	8.6	-2.6
TUL 1014	104070	05/25/2006	-13.1	-96		
TUL 1015	104071	05/23/2006	-10.2	-75		

SWRCB ID	LLNL ID	Collection Date	Water-$\delta^{18}O$ (‰, VSMOW)	Water-$\delta^{2}H$ (‰, VSMOW)	Nitrate-$\delta^{15}N$ (‰, Air)	Nitrate-$\delta^{18}O$ (‰, VSMOW)
TUL 1016	104072	05/23/2006	-8.5	-66		
TUL 1017	104073	05/24/2006	-11.5	-84		
TUL 1019	104074	05/23/2006	-9.3	-66		
TUL 1020	104075	05/25/2006	-11.6	-84		
TUL 1021	104076	05/23/2006	-9.2	-68		
TUL 1022	104077	05/24/2006	-11.2	-83		
TUL 1024	104078	05/25/2006	-8.2	-61		
TUL 1025	104079	05/23/2006	-11.9	-88		
TUL 1026	104080	05/23/2006	-8.5	-63		
TUL 1027	104081	05/23/2006	-12.4	-86		
TUL 1028	104082	05/23/2006	-12.3	-89		
TUL 1029	104083	05/25/2006	-11.9	-83		
TUL 1031	104084	05/24/2006	-13.5	-98		
TUL 1032	104085	05/25/2006	-10.5	-77		
TUL 1033	104086	05/25/2006	-11.5	-85		
TUL 1034	104121	06/08/2006	-11.3	-76		
TUL 1035	104111	06/06/2006	-12.5	-89	4.1	-1.0
TUL 1036	104112	06/06/2006	-12.5	-89	4.6	-2.4
TUL 1038	104087	05/23/2006	-12.0	-90		
TUL 1039	104088	05/24/2006	-11.2	-83		
TUL 1040	104089	05/25/2006	-11.5	-81		
TUL 1041	104122	05/24/2006	-10.5	-75		
TUL 1042	104123	06/07/2006	-11.8	-80		
TUL 1043	104124		-8.5	-67		
TUL 1044	104125	06/08/2006	-12.6	-89		
TUL 1050	104113	06/06/2006	-12.4	-89	4.3	-3.2
TUL 1051	104126	06/07/2006	-11.8	-80		
TUL 1052	104127		-8.5	-67		
TUL 1053	104128	06/07/2006	-8.0	-58		
TUL 1054	104134	06/13/2006	-10.0	-67		
TUL 1055	104135	06/13/2006	-11.9	-87		
TUL 1056	104136	06/13/2006	-12.5	-88		
TUL 1057	104149	06/14/2006	-11.4	-84		
TUL 1058	104150	06/14/2006	-8.5	-64	6.3	4.9
TUL 1059	104151	06/14/2006	-8.4	-65		
TUL 1060	104152	06/15/2006	-11.0	-81		
TUL 1061	104153	06/14/2006	-8.5	-65		
TUL 1062	104154	06/15/2006	-8.6	-65		
TUL 1063	104155	06/14/2006	-9.1	-67		
TUL 1064	104137	06/13/2006	-12.8	-93		
TUL 1065	104138	06/13/2006	-12.0	-87		
TUL 1066	104139	06/13/2006	-12.2	-86		
TUL 1070	104156	06/14/2006	-11.6	-85		
TUL 1071	104140	06/13/2006	-11.7	-85		
TUL 1072	104157	06/14/2006	-9.6	-69		
TUL 1073	104158	06/14/2006	-11.9	-88		
TUL 1074	104159	06/14/2006	-11.2	-80		

SWRCB ID	LLNL ID	Collection Date	Water-$\delta^{18}O$ (‰, VSMOW)	Water-$\delta^{2}H$ (‰, VSMOW)	Nitrate-$\delta^{15}N$ (‰, Air)	Nitrate-$\delta^{18}O$ (‰, VSMOW)
TUL 1075	104160	06/15/2006	-11.7	-84		
TUL 1076	104161	06/15/2006	-11.1	-81		
TUL 1077	104141	06/13/2006	-12.5	-87	5.4	-0.2
TUL 1078	104162	06/14/2006	-9.7	-69		
TUL 1079	104163	06/15/2006	-12.5	-91		
TUL 1080	104164	06/15/2006	-12.3	-84		
TUL 1081	104165	06/15/2006	-11.9	-84	11.2	-1.9
TUL 1082	104166	06/15/2006	-12.6	-89		
TUL 1083	104167	06/15/2006	-12.6	-89		
TUL 1084	104169	06/20/2006	-12.6	-93		
TUL 1085	104170	06/20/2006	-10.9	-79		
TUL 1086	104171	06/20/2006	-9.7	-67		
TUL 1087	104172	06/20/2006	-8.9	-65		
TUL 1088	104173	06/20/2006	-8.2	-61		
TUL 1089	104174	06/20/2006	-10.3	-77		
TUL 1090	104180	06/21/2006	-7.5	-59		
TUL 1091	104181	06/21/2006	-7.6	-60		
TUL 1092	104182	06/21/2006	-11.2	-84		
TUL 1093	104183	06/21/2006	-9.8	-72		
TUL 1094	104184	06/21/2006	-9.0	-62		
TUL 1095	104185	06/21/2006	-9.8	-70		
TUL 1096	104190	06/22/2006	-8.4	-61		
TUL 1097	104191	06/22/2006	-9.9	-71		
TUL 1098	104186	06/21/2006	-11.8	-85		
TUL 1099	104192	06/22/2006	-8.4	-63		
TUL 1100	104175	06/20/2006	-9.0	-62		
TUL 1101	104193	06/22/2006	-6.2	-52		
TUL 1103	104176	06/20/2006	-12.5	-89		
TUL 1104	104194	06/22/2006	-9.5	-67		
TUL 1105	104177	06/20/2006	-11.1	-81	8.2	1.4
TUL 1106	104195	06/22/2006	-12.3	-87		
TUL 1107	104196	06/22/2006	-8.2			
TUL 1108	104178	06/20/2006	-10.9	-80		
TUL 1109	104187	06/21/2006	-9.0	-62		
TUL 1110	104197	06/22/2006	-9.5	-66		
TUL 1111	104198	06/22/2006	-9.5	-72	7.2	3.1
TUL 1201	103902		-12.1	-87		
TUL 1202	103925	04/20/2006	-11.3	-79		
TUL 1205	103914	04/19/2006	-11.4	-82		
TUL 1505	104090	06/08/2006	-10.0	-70	3.7	4.2

SAMPLE QA/QC DATA

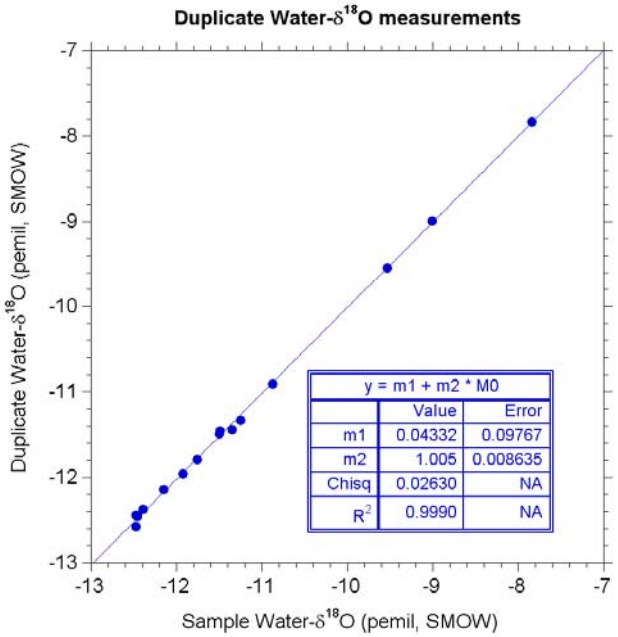
Field duplicate data are tabulated in Table 4. For the two nitrate field duplicates, nitrate-$\delta^{15}N$ analyses agreed to better than 0.3‰, and nitrate-$\delta^{18}O$ analyses agreed to better than 0.8‰. For the 15 water field duplicates, water-$\delta^{18}O$ analyses agreed to within 0.1‰. Water-$\delta^{2}D$ analyses agreed to 2‰ or better with the exception of three samples which agreed to within 4‰. The agreement between the original and duplicate water isotopic composition determinations is shown in Figure 1.

Table 4: Isotopic Composition Analyses of Field Duplicates

SWRCB ID	LLNL ID	Collection Date	Water-$\delta^{18}O$ (‰, SMOW)	Water-$\delta^{2}H$ (‰, SMOW)	Nitrate-$\delta^{15}N$ (‰, Air)	Nitrate-$\delta^{18}O$ (‰, SMOW)
TUL0945	103977	4/27/06	-7.8	-63		
TUL0957	103979	4/27/06	-7.8	-63		
TUL0992	104035	5/18/06	-11.5	-81		
TUL1004	104047	5/18/06	-11.5	-82		
TUL0941	103960	4/25/06	-12.4	-86	8.2	-0.3
TUL0954	103964	4/26/06	-12.4	-88	8.1	-0.8
TUL1104	104194	6/22/06	-9.5	-67		
TUL1110	104197	6/22/06	-9.5	-66		
TUL1036	104112	6/6/06	-12.5	-89	4.6	-2.4
TUL1050	104113	6/6/06	-12.4	-89	4.3	-3.2
TUL1079	104163	6/15/06	-12.5	-91		
TUL1083	104167	6/15/06	-12.6	-89		
TUL0906	103898		-12.2	-87		
TUL1201	103902		-12.1	-87		
TUL1056	104136	6/13/06	-12.5	-88		
TUL1077	104141	6/13/06	-12.5	-88		
TUL1033	104086	5/25/06	-11.5	-85		
TUL1040	104089	5/25/06	-11.5	-81		
TUL1042	104123	6/7/06	-11.8	-80		
TUL1051	104126	6/7/06	-11.8	-80		

SWRCB ID	LLNL ID	Collection Date	Water-$\delta^{18}O$ (‰, SMOW)	Water-$\delta^{2}H$ (‰, SMOW)	Nitrate-$\delta^{15}N$ (‰, Air)	Nitrate-$\delta^{18}O$ (‰, SMOW)
TUL0927	103923	4/20/06	-11.3	-79		
TUL1202	103925	4/20/06	-11.3	-79		
TUL0911	103906	4/19/06	-11.4	-81		
TUL1205	103914	4/19/06	-11.4	-82		
TUL1094	104184	6/21/06	-9.0	-62		
TUL1109	104187	6/21/06	-9.0	-62		
TUL1025	104079	5/23/06	-11.9	-88		
TUL1038	104087	5/23/06	-12.0	-91		
TUL1085	104170	6/20/06	-10.9	-79		
TUL1108	104178	6/20/06	-10.9	-80		

Note: Samples TUL0945 and TUL0957 are not true field duplicates. These are samples from the same well collected approximately two weeks apart.



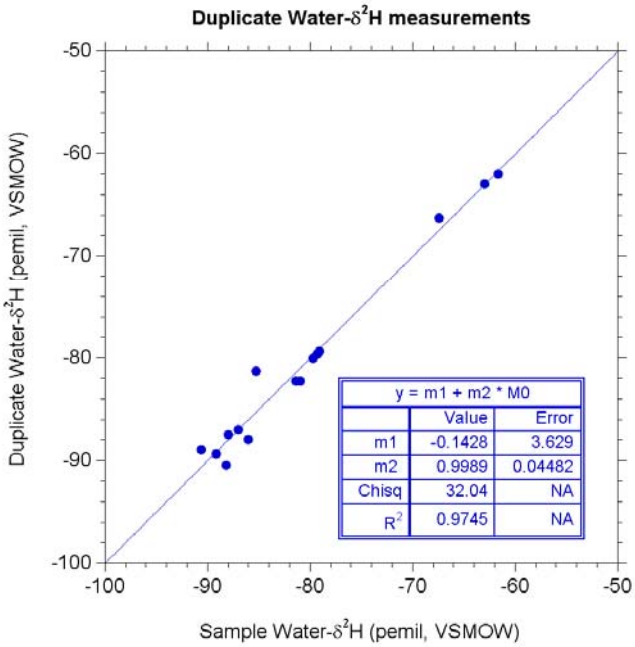


Figure 1. Plot of field duplicate water isotopic composition measurement against sample water isotopic composition measurements.

Discussion and Interpretation

ANALYSES

The spatial distribution of sampling for nitrate concentration, isotopic composition of water and isotopic composition of nitrate is shown in Figure 2.

Approximately 204 samples (including duplicates) were collected from domestic wells in Tulare County for the State Water Board GAMA Domestic Wells Project. These wells had NO_3 concentrations ranging from 0.8 to 240 mg/L as NO_3. The highest nitrate concentrations were observed from wells located in the valley and along the margin of the foothills. Above 1000 ft elevation, only two samples had nitrate concentrations above the MCL.

A majority (151) of the samples from the Tulare County Private Domestic Well study area were analyzed for O and H isotope compositions of water. A small number (29) of samples were analyzed for the isotopic composition of N and O isotopic compositions of nitrate. The small number of nitrate isotopic samples analyzed were biased toward waters containing high concentrations of nitrate (median and mean of 23 and 49 mg/L as nitrate versus 12 and 26 mg/L for the entire sample set). The isotopic composition of water for samples analyzed for nitrate isotopic composition was not significantly different than for the entire data set (mean $\delta^{18}O$-H_2O of -10.8‰ versus -10.4‰ for the entire data set).

ISOTOPIC COMPOSITION OF WATER

A total of 151 samples were analyzed for O and H isotope compositions of water from the Tulare County Private Domestic Well study area. A large range in both $\delta^{18}O$ and δD is observed, from a very light $\delta^{18}O$ value of -13.5‰ to a rather heavy $\delta^{18}O$ of -6.2‰ (Figure 3).

Typically for stable isotopes of water, there is a correlated decrease in the isotopic composition of precipitation with increasing elevation. In the Sierra, this correlation has been observed to be approximately -2.3‰ in $\delta^{18}O$-H_2O per kilometer of elevation (Figure 4; Rose et al., 1996). This general pattern is observed in GAMA Private Domestic Well study results from El Dorado County, where lighter signatures (more negative $\delta^{18}O$ values) were observed with increasing elevation and heavier signatures (less negative $\delta^{18}O$ values) were observed in the valley floor, indicating the predominance of locally-derived water in the domestic wells sampled. The Tulare County pattern is distinctly different (Figure 5). Many of the samples collected from lower elevations have *lower* $\delta^{18}O$-H_2O and $\delta^{2}H$-H_2O values than would be predicted for precipitation at those elevations (Figure 4).

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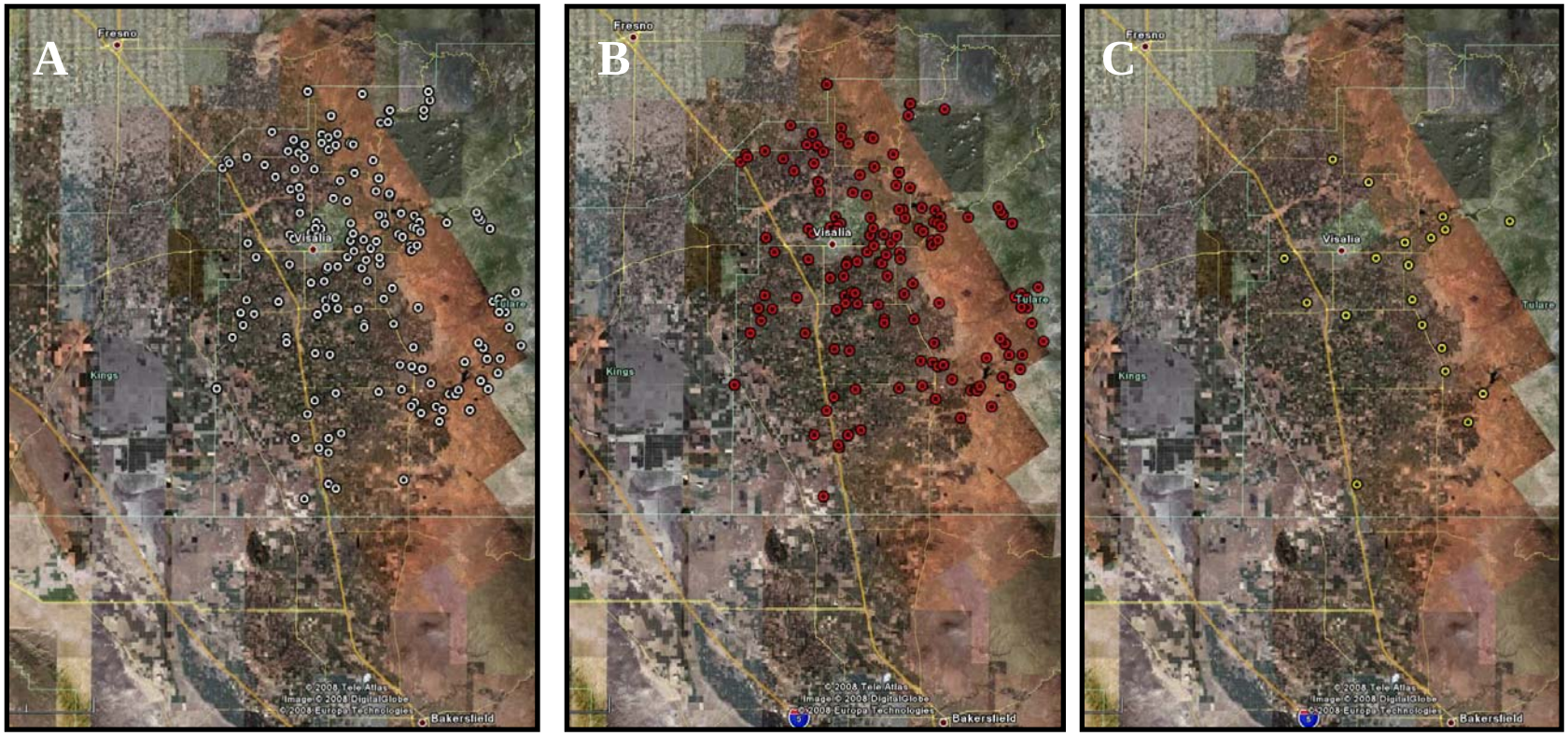


Figure 2. Distribution of domestic wells sampled (A) domestic well water analyzed for water isotopic composition (B), and domestic well waters analyzed for nitrate isotopic composition (C) in the State Water Board GAMA Domestic Well Project.

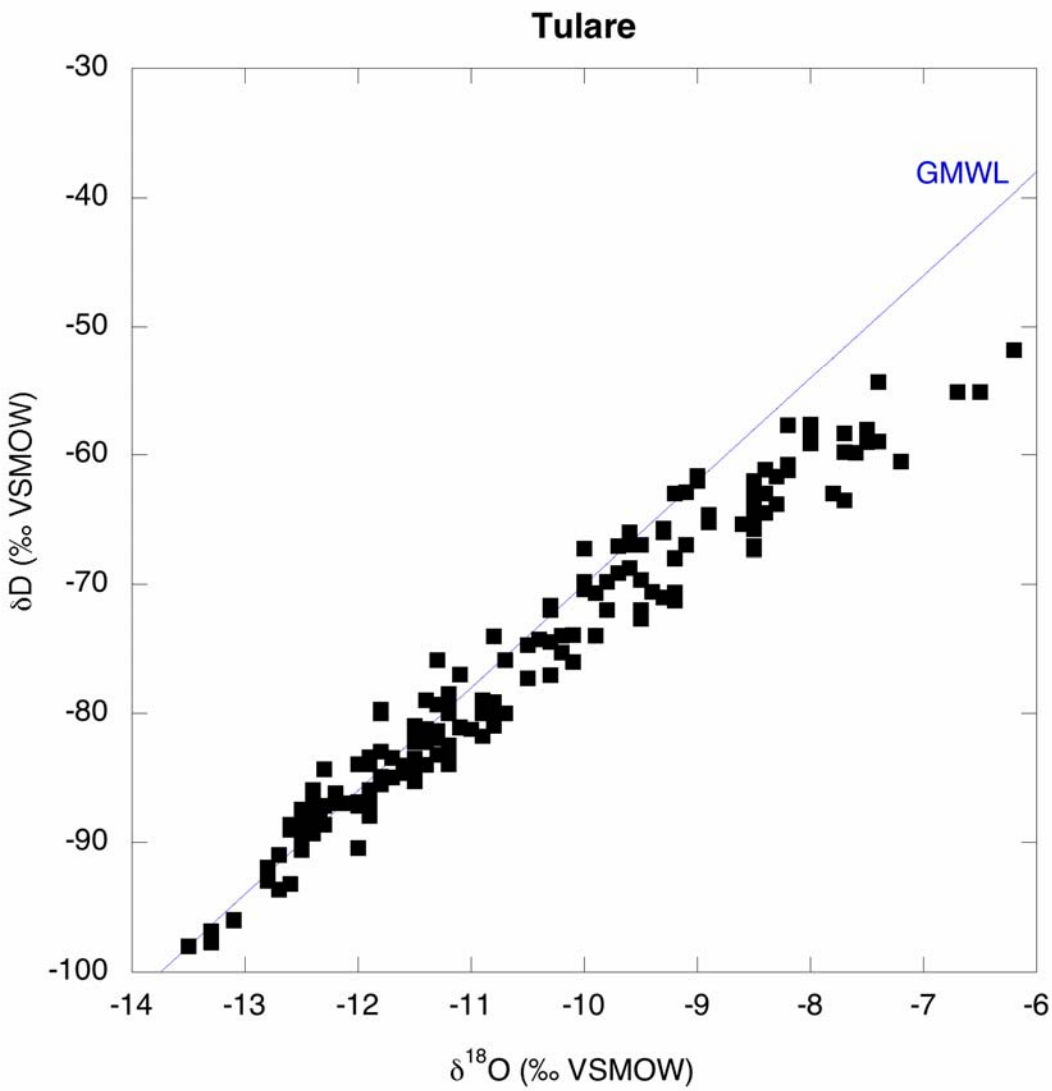


Figure 3. Stable isotope plot for samples from Tulare County Private Domestic wells. The most depleted (most negative) ratios observed are typical for Sierran River runoff sourced at high elevation. Enriched ratios (less negative) show evidence for evaporation, plotting below the meteoric water line.

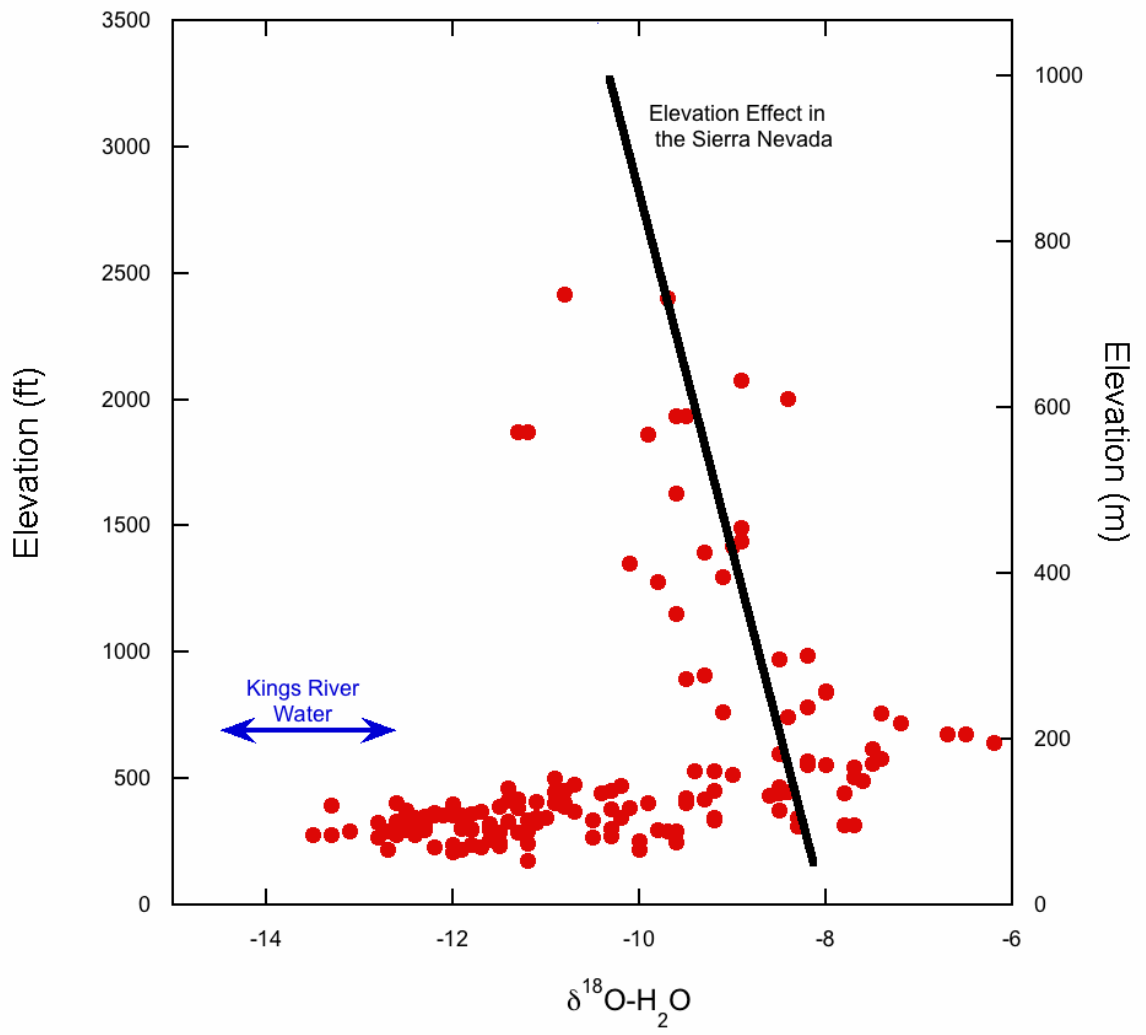


Figure 4. The elevation and oxygen isotope composition of waters collected from Tulare County domestic wells. The solid line shows the observed relation between elevation and $\delta^{18}O\text{-}H_2O$ in the Sierra (Rose et al., 1996). The observed range of Kings River water is shown based on data from Coplen and Kendall (2000).

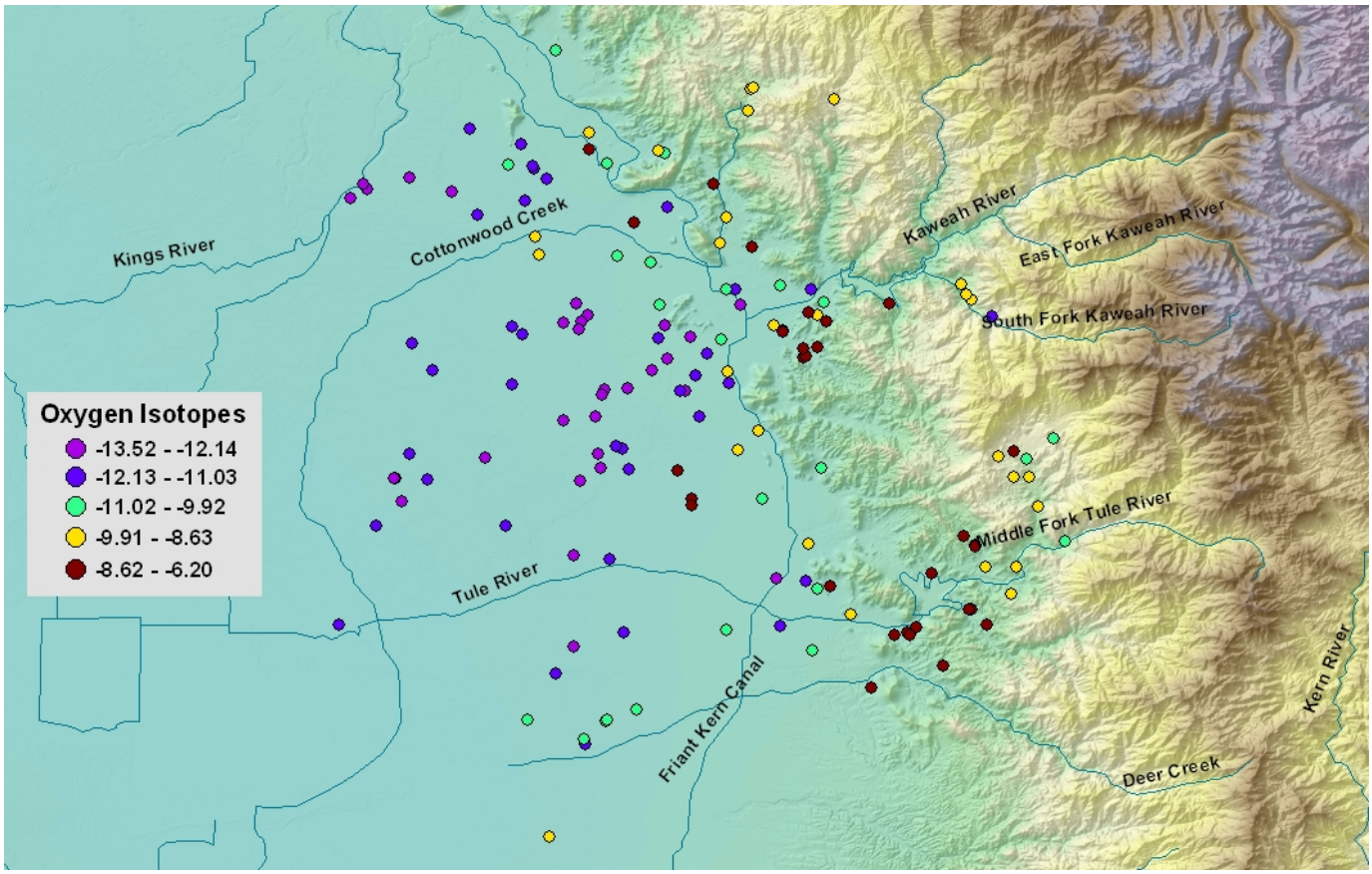


Figure 5. Results of oxygen isotope analyses of water from **Tulare County** domestic wells.

This apparent discrepancy is caused by extensive use of imported water from the Kings and Kaweah Rivers, which are fed from the upper Sierra. This water is used for irrigation, and recharges the shallow aquifer. Coplen and Kendall (2000) report $\delta^{18}O$-H_2O values in the Kings River at Trimmer (elev. 942 ft RMSL) that range from -14.6 to -12.5 ‰, with an average value of -13.3 ‰. The low $\delta^{18}O$-H_2O and $\delta^{2}H$-H_2O values in samples collected from domestic wells on the valley floor (Figures 4 and 5) indicate that these wells tap groundwater that is a mix of irrigation return water and locally derived precipitation. The extent of King's river water present in parts of the Tulare County valley groundwater system may be up to 100 percent.

The excess irrigation water has not experienced significant evaporation, despite the fact that it is applied mainly during summer months. Infiltration must take place relatively quickly after application. Evidence for lack of evaporative effects on these isotopically light samples comes from a plot of $\delta^{18}O$ vs. δD (figure 3). Samples with isotope pairs that fall below the global meteoric water line (GMWL) have experienced significant evaporation, but for Tulare samples, only samples with $\delta^{18}O$ values greater than -9‰ show an evaporation effect. Samples with water $\delta^{18}O$ values greater than -9‰ are found on the eastern side of the study area, primarily in the foothills (Figures 4 and 5). These areas are not surrounded by irrigated agricultural fields, and irrigation return flow is not a likely source of significant recharge. Rather, $\delta^{18}O$ results from wells in the eastern portion of the study area suggest that local precipitation is the main source of recharge and that evaporation prior to recharge affects some wells. The $\delta^{18}O$ value for precipitation in the Tulare County valley area is predicted to be approximately -7.5‰ to -8‰. A pattern of decreasing $\delta^{18}O$ with increasing elevation within the foothill samples is evident in figure 3. This is further evidence that recharge to wells in the foothill area is mainly from locally derived precipitation.

ISOTOPIC COMPOSITION OF NITRATE

The nitrate N and O isotope data set consists of 29 distinct samples (plus two duplicates), and is small relative to the total set of samples collected (n=203 including 22 duplicates). Of the samples analyzed for N and O isotope compositions, only two samples are from wells above 800 ft elevation (Figure 6). Most samples are collected from the valley and the margins of the foothills (Figures 7 and 8). We have delineated the sample set into two groups based on elevation (Figures 6): the valley wells (<400 ft. MSL) and the foothills and margins of the foothills (>400 ft. MSL). In general, these two areas are distinct in both hydrogeology and land use. The valley wells are located in the thick alluvial fan deposits, while the margin/foothills wells are more likely to overly a thinner sequence of alluvium and bedrock. Dairy operations, orchards and row crops are densely distributed at the valley elevations, while the margins and upper foothills are commonly planted with orchards. Most of Tulare County's population (which can be used as a proxy for septic effluent sources of nitrate) is located below 400 feet.

Seven samples that were analyzed for nitrate N and O isotopic composition had nitrate concentrations over the MCL. These seven samples with high NO_3 concentration have $\delta^{15}N$-NO_3 values that range from 3.7 to 11.2 ‰, with an average of 6.9 ‰. Nitrate $\delta^{15}N$-NO_3 values in this range are typically consistent with nitrification of ammonium from human waste or animal waste, i.e. septic effluent or dairy manure (see Figure 9).

The highest concentration sample, TUL 0979, was 240 mg/L-NO3 and had a $\delta^{15}N\text{-}NO_3$ value of 6.1 and a $\delta^{18}O\text{-}NO_3$ value of 8.2 (Figure 6-7) The isotopic composition of nitrate in TUL 0979 is generally consistent with containing a component of nitrate or mixed nitrate/ammonium synthetic fertilizer (Figure 9). Nitrate in TUL 0928 also has an isotopic composition consistent with synthetic nitrate, but its nitrate concentration is low (1.6 mg/L NO3).

In general, the oxygen isotope composition of nitrate ($\delta^{18}O\text{-}NO_3$) produced by nitrification of ammonium is correlated with the oxygen isotope composition of local water ($\delta^{18}O\text{-}H_2O$). This correlation is due to incorporation of local water and atmospheric oxygen, typically in a 2:1 ratio, during production of nitrate from ammonium from either synthetic ammonium fertilizer or animal/human waste. The relation of oxygen isotope compositions in nitrate and water for Tulare County domestic wells is shown in Figure 10. Lines showing the predicted nitrate and water $\delta^{18}O$ values produced from nitrification of ammonium are also plotted, with a range reflecting uncertainty in the local pore water $\delta^{18}O$ values in the unsaturated zone where nitrification is most likely to occur. Most samples have nitrate and water $\delta^{18}O$ values that are consistent with nitrification of ammonium in the presence of local water. Samples from the valley fall lower on the plot and reflect nitrification of ammonium in the presence of the irrigation return water with low $\delta^{18}O\text{-}H_2O$. Mixing with synthetic NO_3 fertilizer would cause samples to fall above the predicted lines.

Coplen, T. B. and Kendall, C., 2000. Stable Hydrogen and Oxygen Isotope Ratios for Selected Sites of the U.S. Geological Survey's NASQAN and Benchmark Surface-water Networks. USGS Open-File Report 00-160.

Kendall, C., 1998. Tracing nitrogen sources and cycling in catchments. In: Kendall, C. and McDonnell, J. J. Eds.), *Isotope Tracers in Catchment Hydrology*. Elsevier, New York.

SWRCB, 2010. GAMA Domestic Well Project Groundwater Quality Data Report: Tulare County Focus Area (Draft). California State Water Resources Control Board Groundwater Protection Section (Groundwater Ambient Monitoring & Assessment Program). http://www.swrcb.ca.gov/gama/domestic_well.shtml.

Rose, T. P., Davisson, M. L., and Criss, R. E., 1996. Isotope hydrology of voluminous cold springs in fractured rock from an active volcanic region, northeastern California. *Journal of Hydrology* **179**, 207-236.

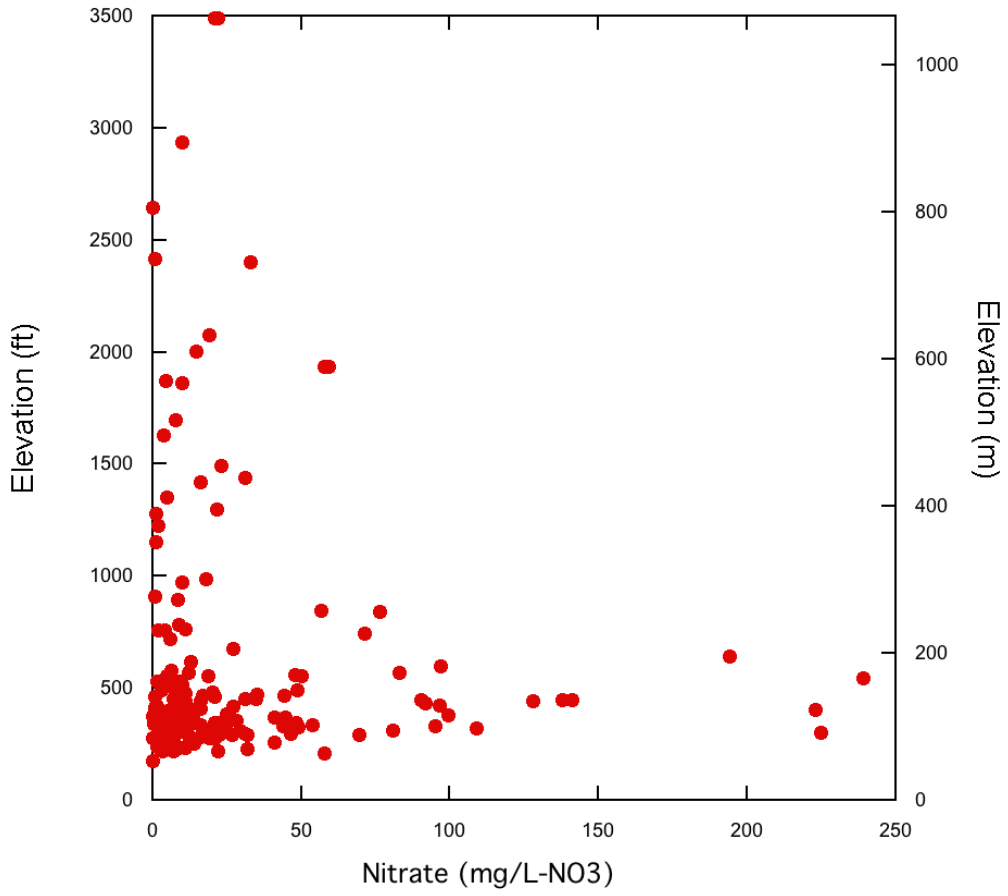


Figure 6. Well elevation versus dissolved nitrate concentrations in Tulare County domestic well samples.

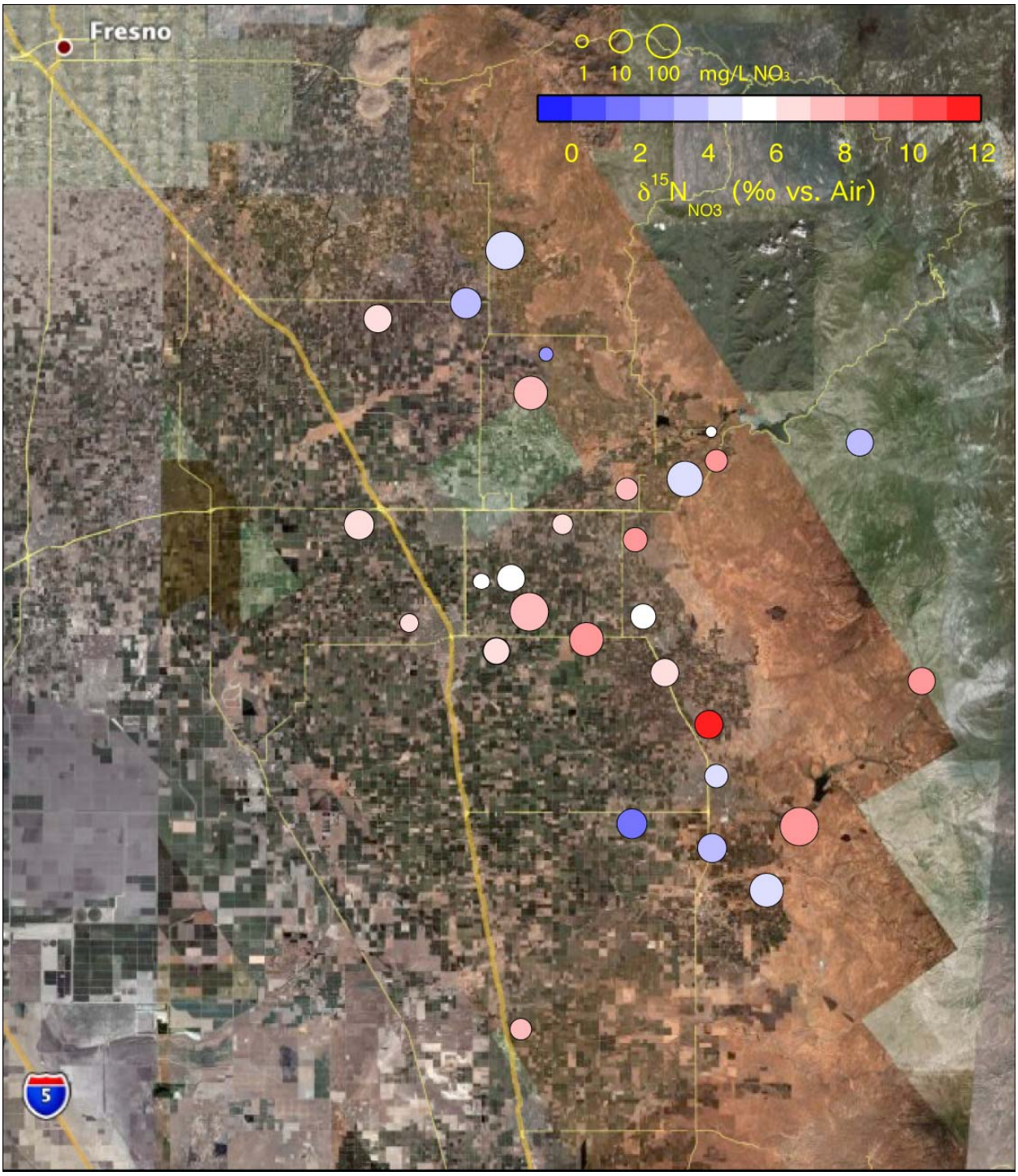


Figure 7. Wells analyzed for N isotope compositions in nitrate are shown on a Google Earth satellite image. The isotopic composition of nitrate-N ($\delta^{15}N$-NO_3) is represented by the color of the dot. The nitrate concentration of each well is represented by the size of the dot.

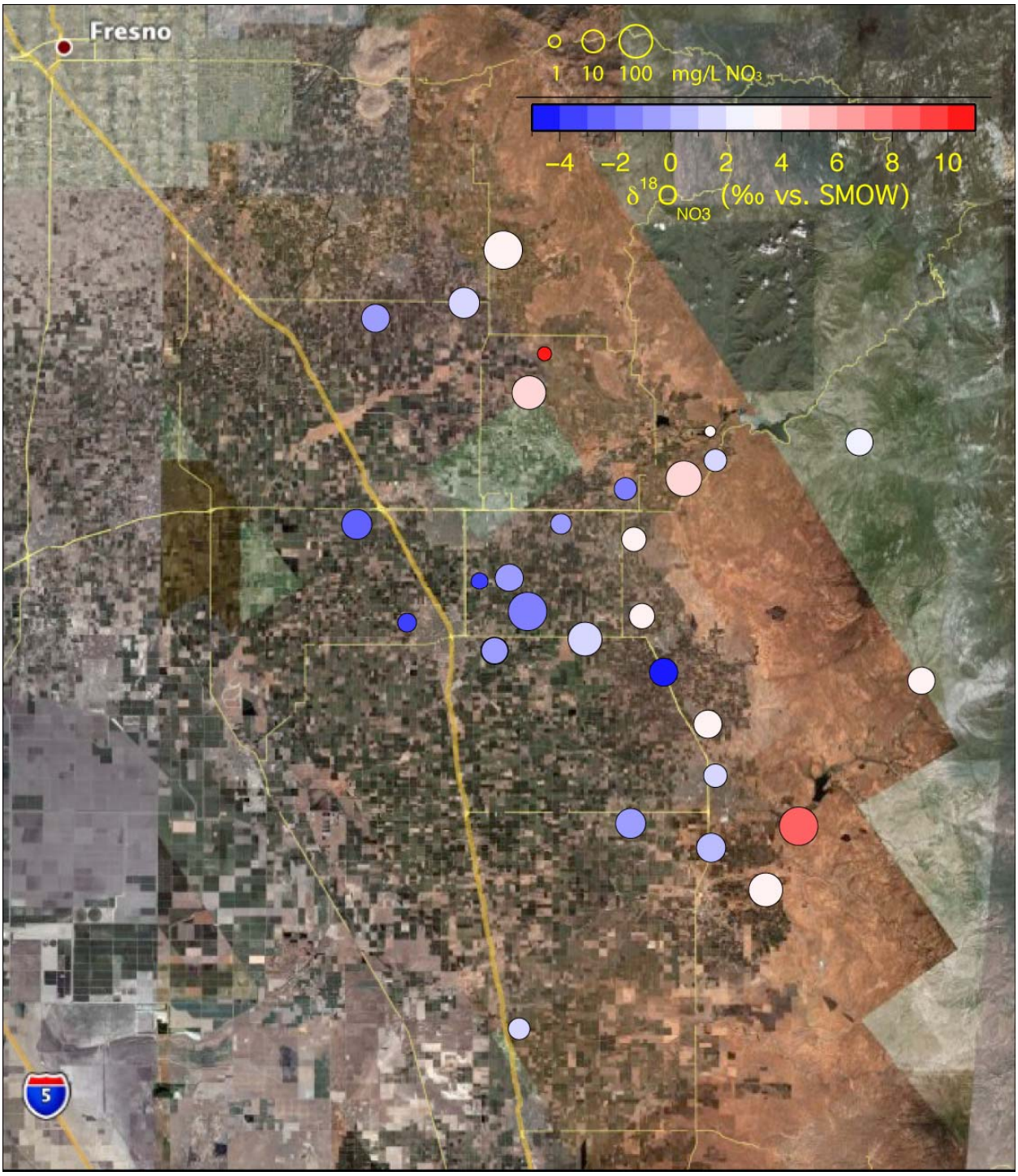


Figure 8. Wells analyzed for O isotope compositions in nitrate are shown on a Google Earth satellite image. The isotopic composition of nitrate-O ($\delta^{18}O$-NO_3) is represented by the color of the dot. The nitrate concentration of each well is represented by the size of the dot.

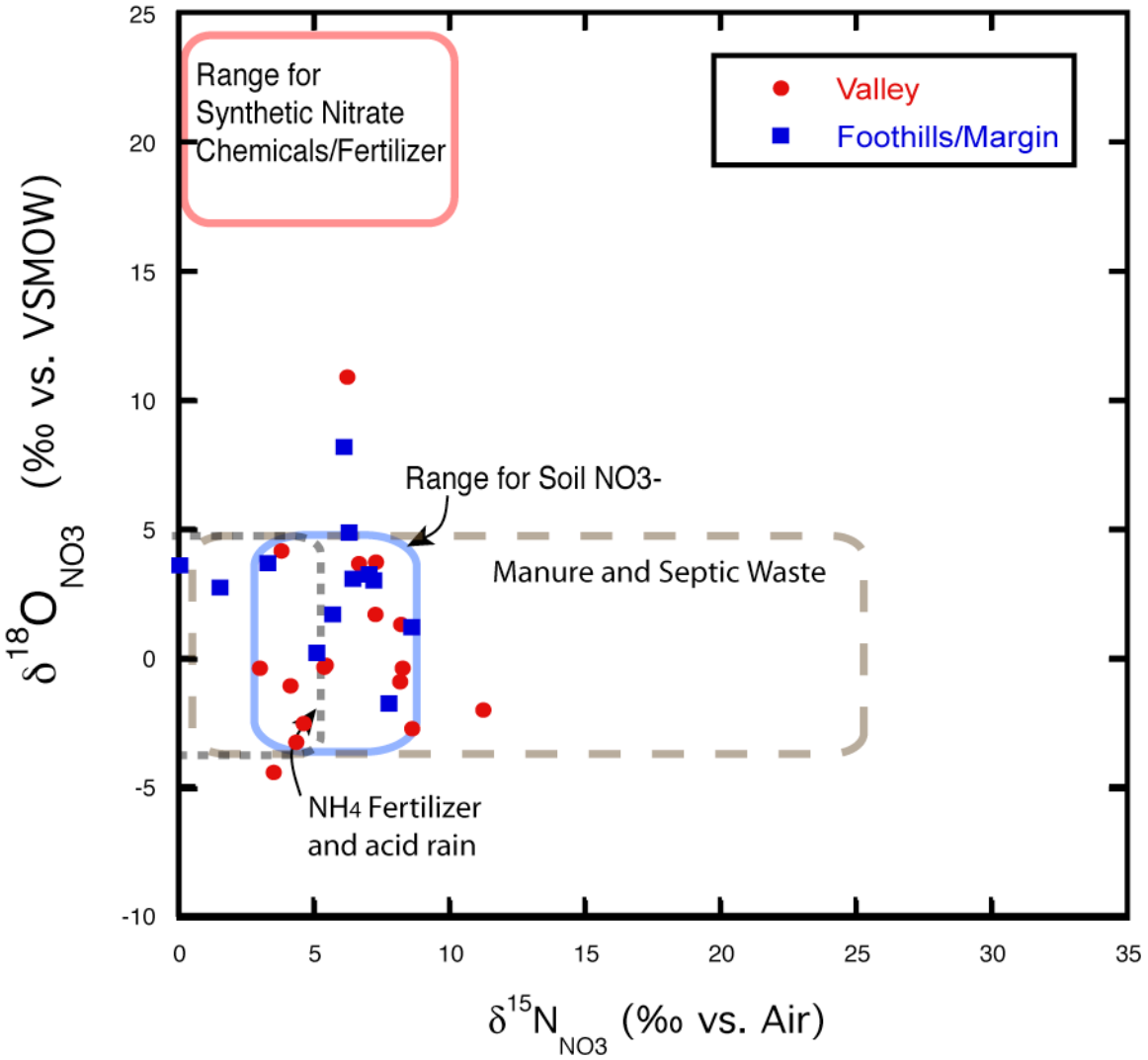


Figure 9. Nitrogen and oxygen isotope compositions of dissolved nitrate in Tulare County wells. Observed ranges from nitrate sources are modified from Kendall (1998) based on the observed oxygen isotope composition of water from this study.

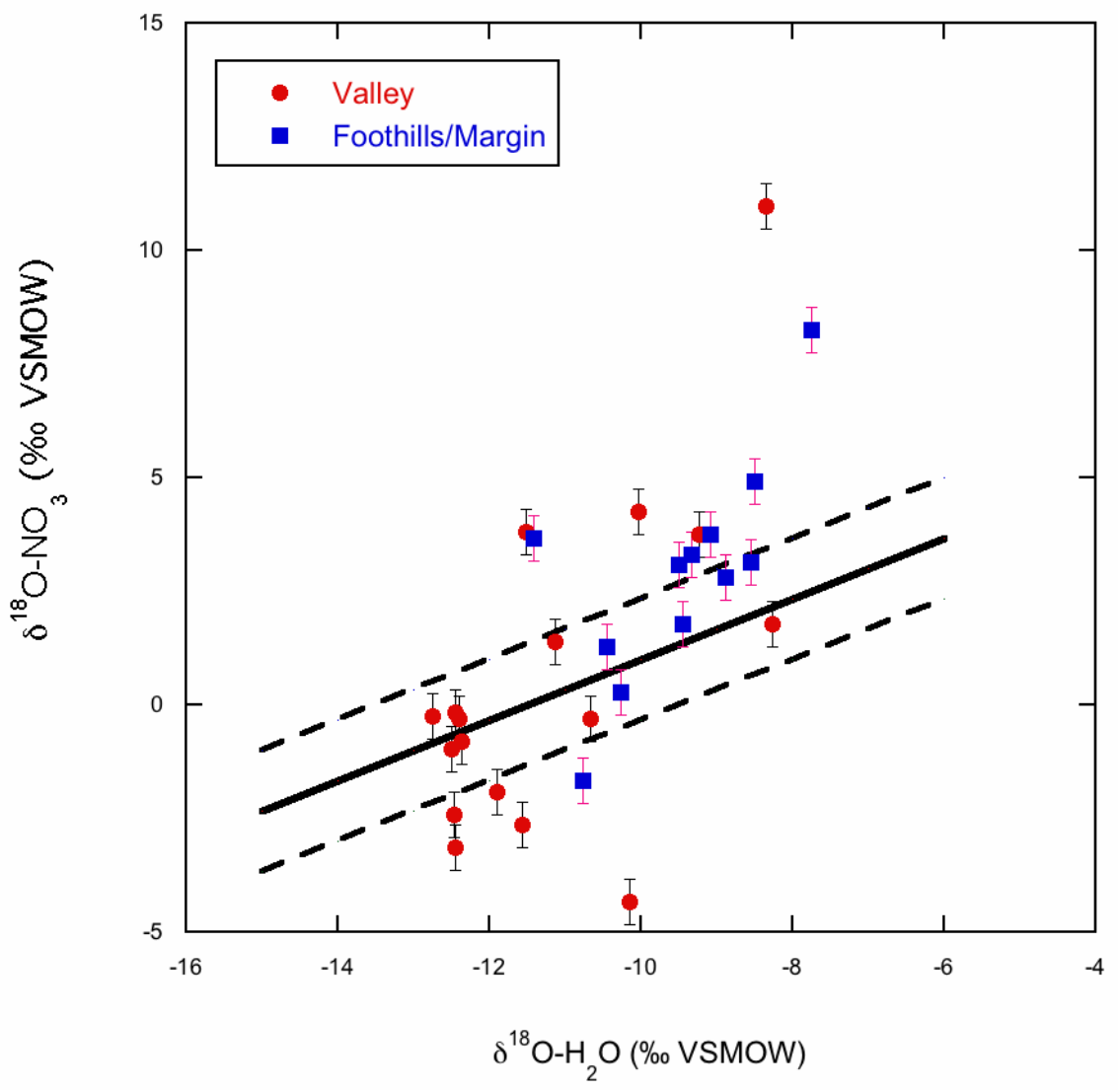


Figure 10. Oxygen isotope compositions in water and nitrate from Tulare County domestic wells. The predicted relation between oxygen isotope compositions in water and nitrate produced by nitrification of ammonium are shown (solid line) with additional lines to account for a range of $\delta^{18}O\text{-}H_2O$ values that may occur in unsaturated zone pore waters where nitrification is likely to occur (dashed lines).

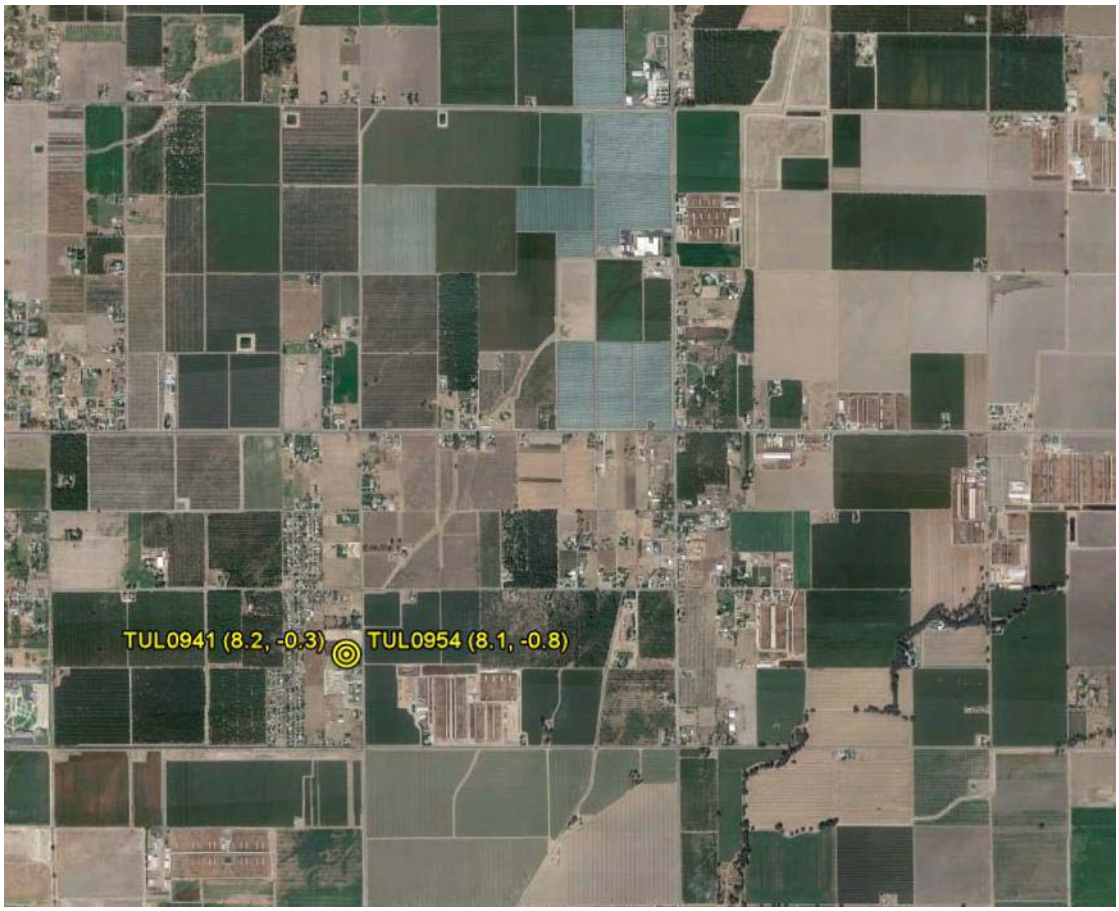


Figure 11. Location of duplicate samples TUL 0941 and TUL 0954 on a Google Earth 2010 satellite image. Both isotopic composition and concentration for these samples reproduced well: 19 vs. 21 mg/L nitrate; 8.2 vs. 8.1 ‰ $\delta^{15}N\text{-}NO_3$,, -0.3 vs. -0.8 ‰ $\delta^{18}O\text{-}NO_3$ (TUL 0941 vs TUL 0954).This valley well (elevation 279 feet) is close to two dairy operations, and the groundwaters have nitrate isotopic compositions within the range of nitrate associated with a dairy manure source.

Figure 12. Location of well TUL979 on a Google Earth 2010 satellite image. This foothill well (elevation 546 feet) is in a sparsely populated area surrounded by orchards and has high nitrate concentration (240 mg/L nitrate). The nitrate isotopic composition ($\delta^{15}N\text{-}NO_3$= 6.1, $\delta^{18}O\text{-}NO_3$ = 8.2), in particular the high $\delta^{18}O\text{-}NO_3$, is indicative of a synthetic fertilizer source.

SIGNIFICANT FINDINGS

- The highest domestic well water nitrate concentrations are found in valley wells below 400 feet surface elevation.
- Domestic wells below 400 feet surface elevation draw on groundwater heavily impacted by irrigation with Kings and Kaweah River water, as indicated by water isotopic composition. This finding is consistent with both the long and heavy usage of Kings River water for irrigation in this area, and with the assumed shallow depth of these domestic wells. Nitrate associated with these waters is presumably associated with the same source (chemical or organic fertilizer in irrigation water) or is mobilized by irrigation (septic effluent or soil nitrogen).
- Domestic wells in the foothills (with elevations above 400 feet) receive recharge derived from local precipitation that has experienced some evaporation.
- Nitrate concentrations in the most polluted wells are sufficiently high to preclude a significant contribution from soil or atmospheric sources. Such sources cannot be precluded in wells with nitrate concentrations below the regulatory drinking water limit, however the data set does not include enough samples near typical background concentration levels to assess the isotopic characteristics of natural nitrate sources in this area.
- Nitrate isotopic compositions indicate a dairy manure or septic effluent source for the majority of the most heavily impacted wells, with the exception of one well with high nitrate concentration and an isotopic composition indicative of a synthetic fertilizer source. An analysis of land use and the distribution of potential nitrate sources would be extremely useful.

A preliminary investigation of the correlation between land use and nitrate isotopic composition was conducted (see Appendix "GAMA Domestic Well Project - Tulare County. Nitrate Source Attribution: The Isotopic Evidence"). The sparse nitrate isotopic data set is under-represented by domestic wells with no potential anthropogenic sources within 500 m of the well, and the method used to assign land use is cursory. Patterns observed, however, are consistent with multiple anthropogenic sources, including dairy wastewater, septic effluent and synthetic fertilizer.

- Nitrate isotopic composition does appear to vary with land use
  - Dairy, agricultural/residential, and wild-land sites are isotopically distinct
  - Dairy site nitrate-N isotopic data are isotopically consistent with a manure source
  - Nitrate-O isotopic data are isotopically consistent with local nitrification of ammonium (from manure, septic effluent, or synthetic ammonium fertilizer)
- The isotopic evidence is consistent with more than one nitrate source
  - Domestic wells located close to dairies do have a different nitrate isotopic composition than wells not close to dairies in similar hydrogeologic settings.
  - The isotopic compositions measured are consistent with the suspected sources of nitrate to these wells (soil, fertilizer, manure, septic or community wastewater).
  - High concentrations of nitrate occur in all developed land use categories.

Appendix

A presentation to the State Water Board in the summer of 2008

GAMA Domestic Well Project: Tulare County

Nitrate Source Attribution: The Isotopic Evidence

Bradley K. Esser & Michael J. Singleton
Lawrence Livermore National Laboratory
In cooperation with the
California State Water Resources Control Board
Summer 2008

GAMA Domestic Well Project: Tulare County

Nitrate Source Attribution: The Isotopic Evidence

Bradley K. Esser & Michael J. Singleton
Lawrence Livermore National Laboratory
In cooperation with the
California State Water Resources Control Board

Summer 2008

This work was performed under the auspices of the U.S. Department of Energy by the University of California Lawrence Livermore National Laboratory under Contract No. W-7405-Eng-48.

GAMA Domestic Well Project (SWRCB)

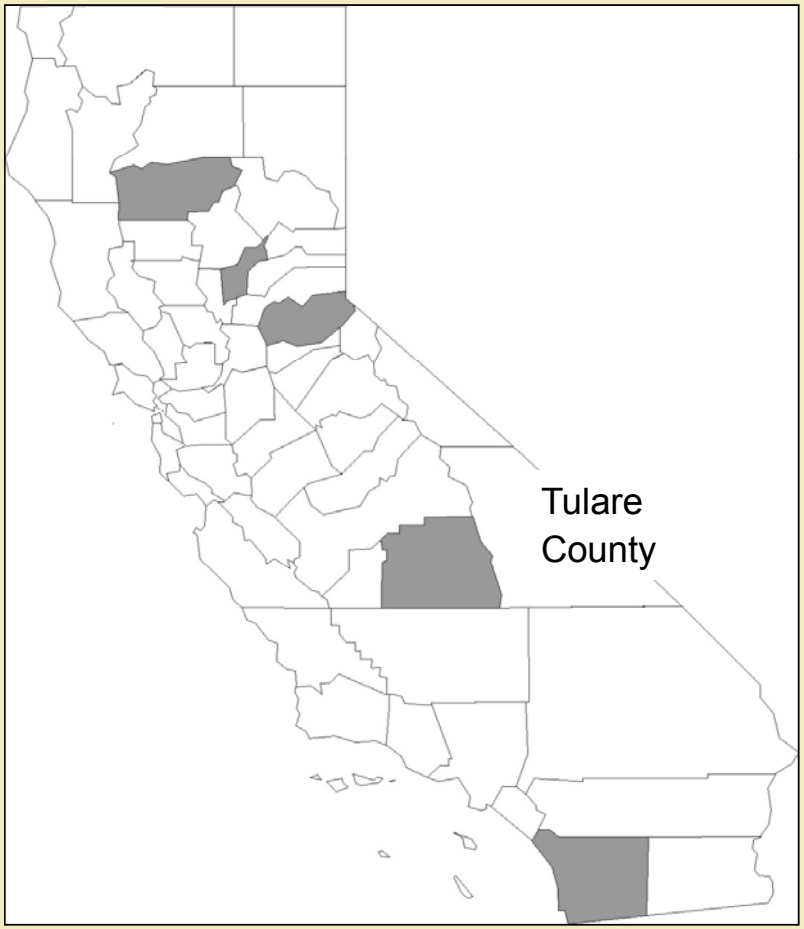
Domestic well water quality in California is largely unknown

- **GAMA Domestic Well Project Goals**
  - To provide specific information on water quality to domestic well owners
  - To provide a public education component to aid the public in understanding water quality issues affecting domestic water wells.
  - To help assess California groundwater quality and identify issues that may impact private domestic well water
- **Water Board is project lead on the Domestic Well Project**
  - Works with local county agencies & regional boards
- **Voluntary program at no cost to well owner**
  - Test results are provided to well owner, whose identities are kept confidential

The Domestic Well project was not designed to test specific hypotheses regarding contaminant sources

Water Boards

State of California GAMA Program Domestic Well Project: Tulare County

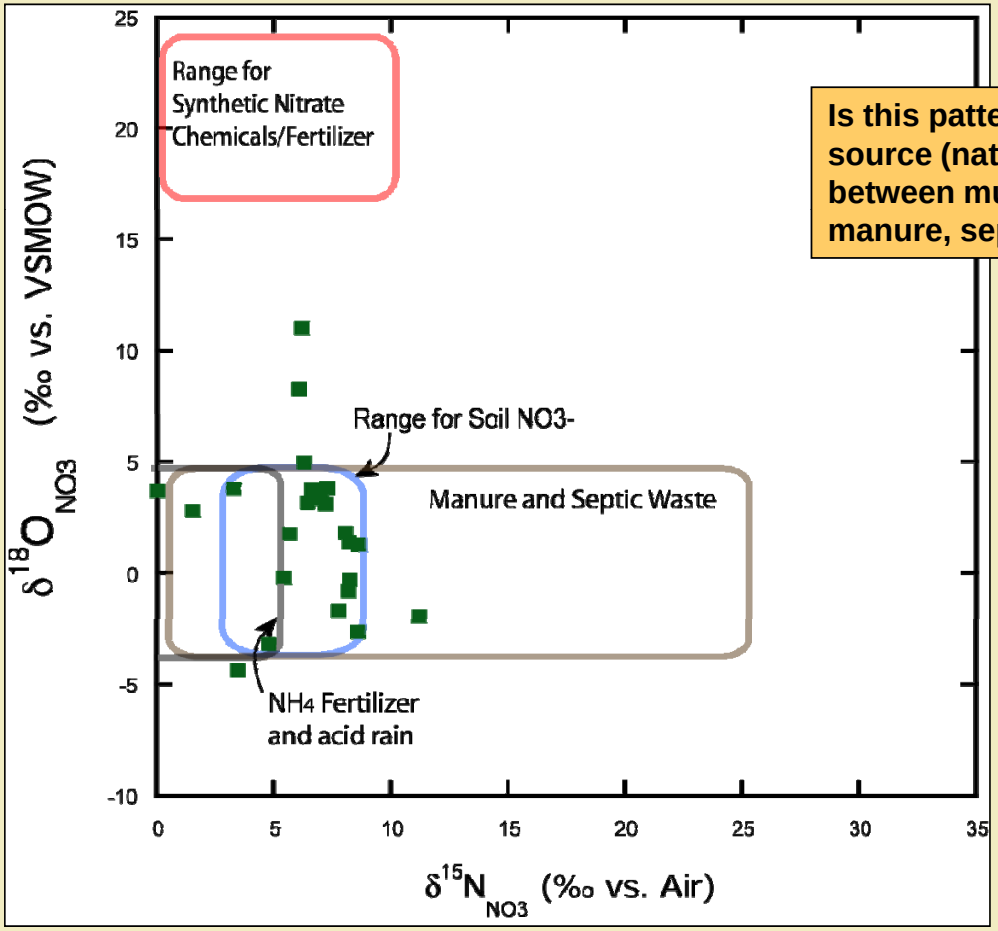


- **Tulare County (2006, n=181)**
  - **More than 40% have nitrate above the MCL**
  - Results are available on the SWRCB website: **http://www.swrcb.ca.gov/gama/voluntary.shtml**

Water Boards

- **LLNL participation**
  - Stable isotopes of water on most wells
  - Stable isotopes of nitrate on a small subset of wells

Nitrate isotopic data on a subset of Tulare County domestic wells does not definitively constrain the nitrate source to these waters



Is this pattern produced by a single source (natural soil N) or by mixing between multiple sources (fertilizer, manure, septic)?

Note: Fields adjusted for local groundwater isotopic composition.

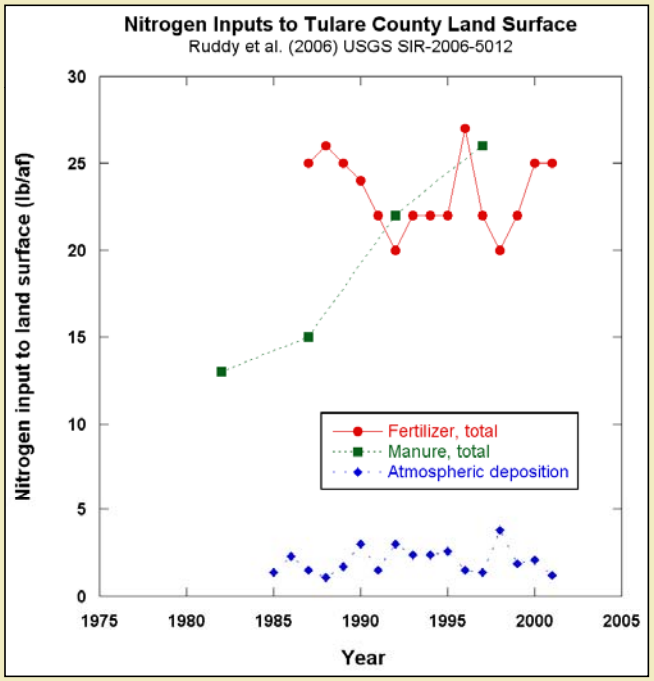
Nitrate in shallow Tulare County groundwater may derive from more than one source, and may be largely anthropogenic

Multiple source hypothesis

- Nitrate in Tulare County shallow groundwater accessed by domestic wells is not from a single natural or anthropogenic source
- Nitrate in Tulare County shallow groundwater derives from some combination of manure, synthetic fertilizer & septic/wastewater discharge

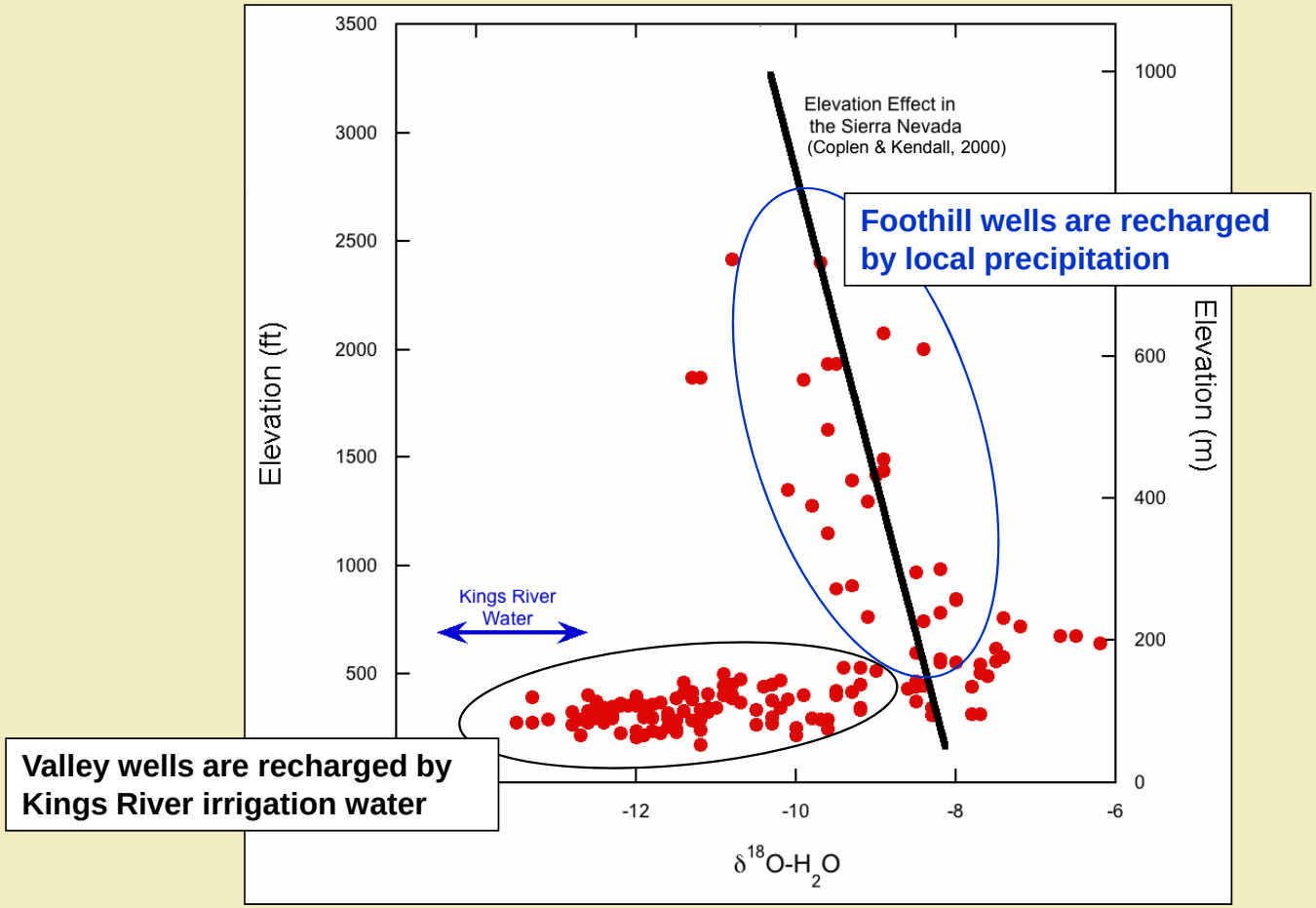
Potential sources

- **Manure & synthetic fertilizer:** Fertilizer records & animal population estimates indicate that sub-equal amounts of fertilizer & manure N are currently being applied to land surface in Tulare County.
- **Wastewater discharge:** Tulare County population (a proxy for septic & wastewater discharge) grew by 50% from 1980 to 2000

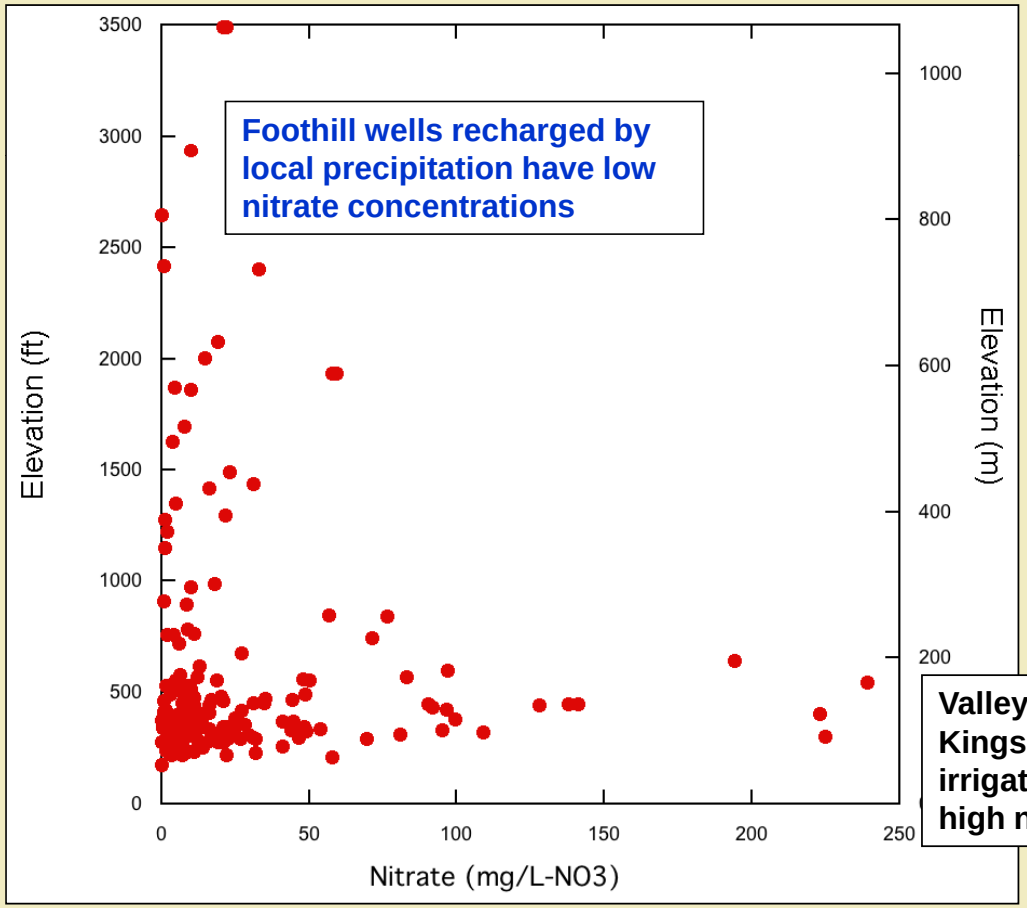


Ruddy, B. C., Lorenz, D. L., and Mueller, D. K., 2006. County-Level Estimates of Nutrient Inputs to the Land Surface of the Conterminous United States, 1982–2001. US Geological Survey, Scientific Investigations Report 2006-5012.

The isotopic composition of water in domestic wells constrains the source of recharge as local precipitation or irrigation



Nitrate concentrations in domestic wells is lower in foothill wells (>400 ft) than in valley wells (<400 ft)



Valley wells recharged by Kings or Kaweah River irrigation water have low to high nitrate concentrations

A simple test:
Does nitrate isotopic composition correlate with land use?

Questions to test the multiple source hypothesis

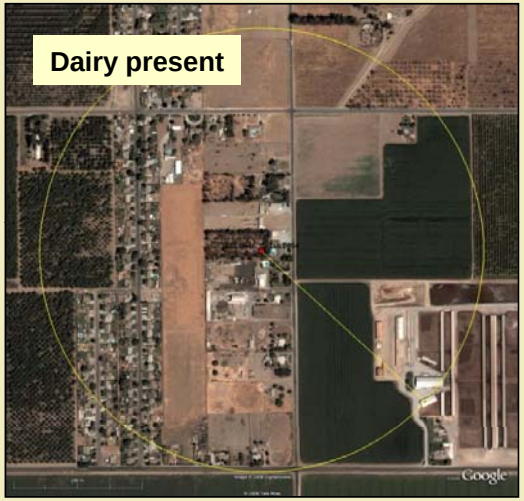
- Do domestic wells located close to dairies have a different nitrate isotopic composition than wells not close to dairies in similar hydrogeologic settings?
- Are the isotopic compositions measured consistent with the suspected sources of nitrate to these wells (soil, fertilizer, manure, septic or community wastewater)?

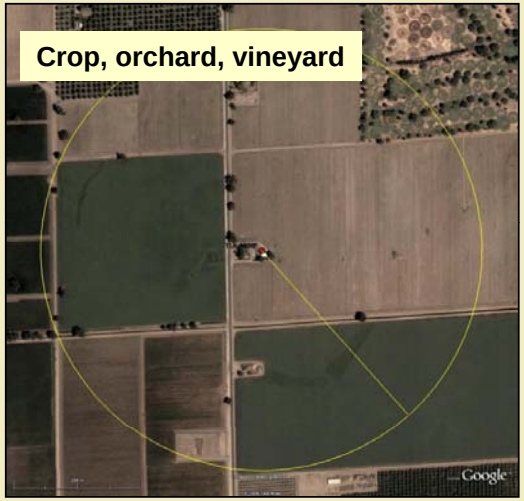
If the answer to these questions is yes,
then the data support the hypothesis that multiple sources of nitrate impact shallow groundwater accessed by Tulare County domestic wells.

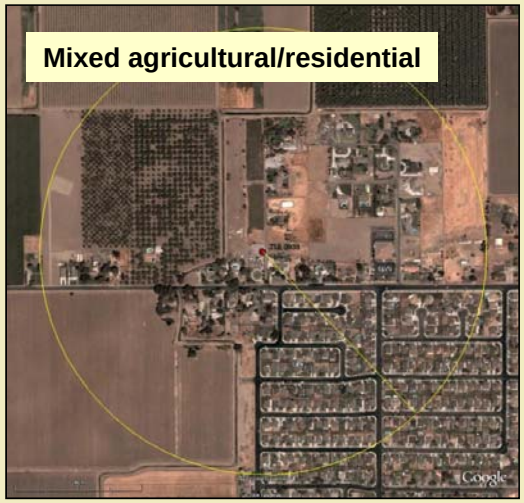
Bottom line: Data are consistent but not definitive for the multiple source hypothesis.
Sparse data set and simplistic approach to assigning land use limit conclusions, but patterns observed are suggestive.

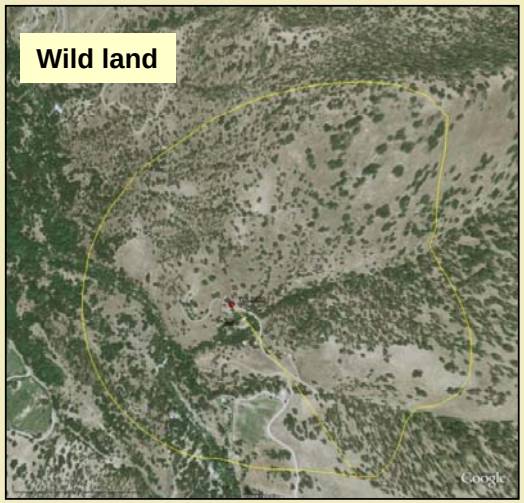
Land use within 500-m of a domestic well

(Source: Google Earth, Imagery from 2004/2005)

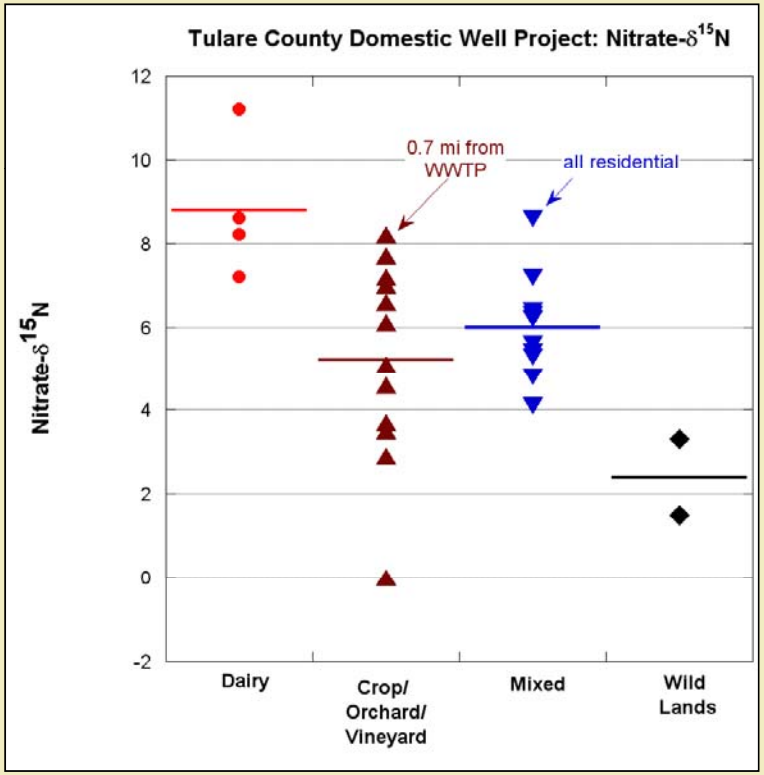








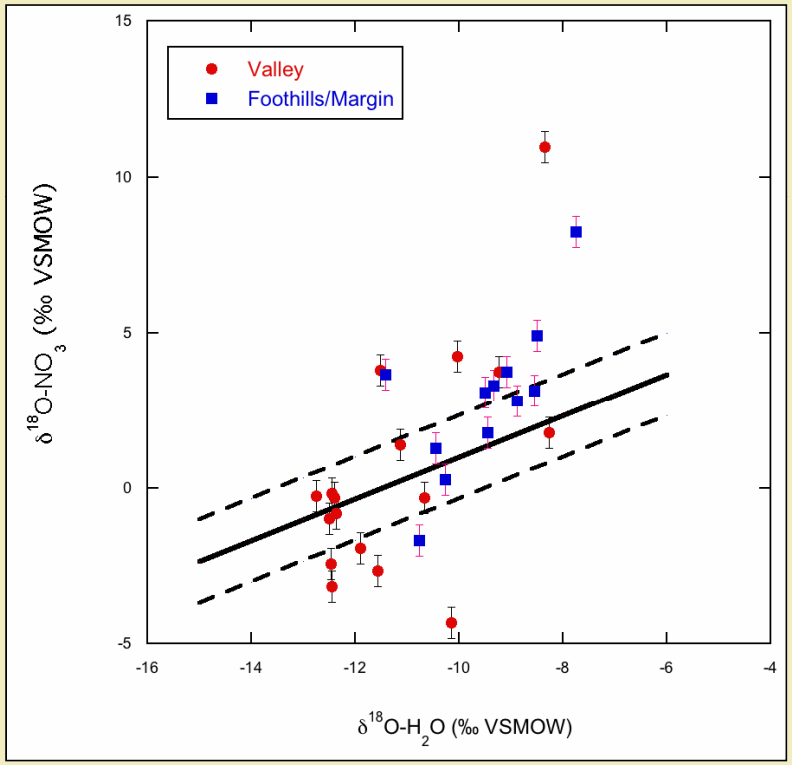
The nitrate isotopic composition of domestic well water in Tulare County is influenced by land use



- **Tentative observations on nitrate isotopic composition**
  - Clear distinction between "dairy" and non-dairy sites, and between "wild land" and agricultural/residential sites
  - Dairy site groundwaters have "manure"-like nitrate-δ^{15}N
- Caveats
  - Very limited sample set, especially for "dairy" and "wild lands" and for low-nitrate well waters
  - Snapshot of land use in complex region; does not account for recent changes (e.g. housing development)
  - Many domestic well owners will have a septic system on site
  - Nitrogen source for row crops, orchards, and vineyards may be organic and/or synthetic fertilizer
  - Foothill "wild land" sites will have different soil type than valley agricultural & residential sites & may not represent natural N for these sites

The correlation between isotopic data and land use is more consistent with multiple anthropogenic sources of nitrate than with a natural soil source

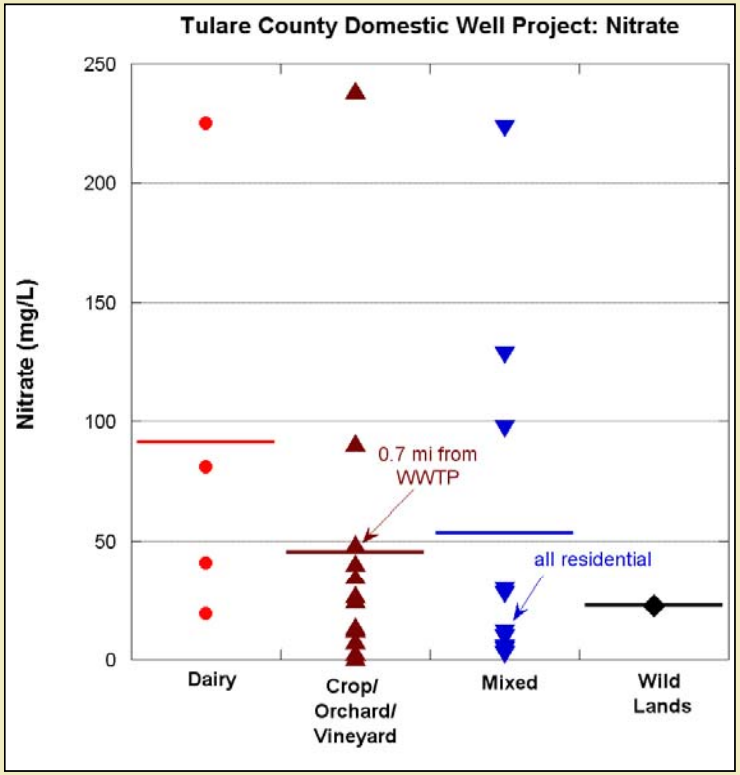
The isotopic composition of nitrate-O is consistent with nitrification of ammonium (from either manure, septic, or fertilizer) with local waters



Oxygen isotope compositions in water and nitrate from Tulare County domestic wells.
The predicted relation between oxygen isotope compositions in water and nitrate produced by nitrification of ammonium are shown (solid line) with additional lines to account for a range of δ18O-H2O values that may occur in unsaturated zone pore waters where nitrification is likely to occur (dashed lines).

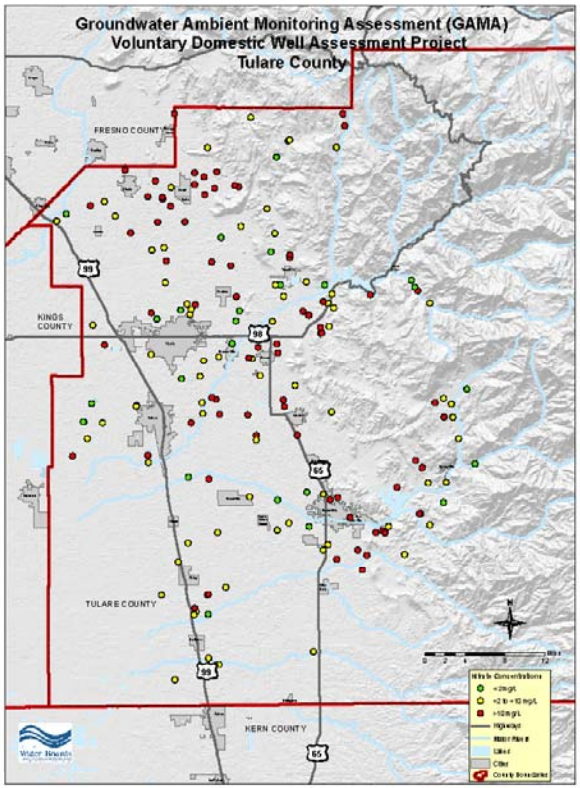
Values that fall significantly off the nitrification trend may derive from synthetic nitrate fertilizer, atmospheric nitrate, or old soil nitrogen equilibrated with local precipitation from before extensive irrigation with Kings River water

Nitrate concentration data indicate potential for shallow groundwater contamination in association with all developed land use categories



- **Tentative observations on nitrate concentration**
  - High concentrations of nitrate (>5x mcl) occur in all developed land use categories
  - Data not sufficient to discern differences in nitrate impact on shallow groundwater with land use
- **All the same caveats apply**
  - Very limited sample set, especially for “dairy” and “wild lands”, and low-nitrate well waters
  - Snapshot of land use in complex region; does not account for recent changes (e.g. housing development)
  - Many domestic well owners will have a septic system on site
  - Nutrient source for row crops, orchards, and vineyards may be organic and/or synthetic fertilizer
  - Wild land sites will have different soil type than agricultural sites

Nitrate concentration and isotopic composition data are consistent with multiple sources of high nitrate to Tulare County domestic wells



- **Future work in Tulare County**
  - Tulare County Water Commission initiatives
  - Thomas Harter Proposition 50 Dairy Project domestic well survey
- **Tulare County as a testbed for source attribution**
  - Pervasive shallow groundwater contamination
  - Valley to foothill environments with different agricultural practices and land use patterns
  - Dairy, irrigated agriculture, septic and community wastewater discharge all present
  - Tulare County Water Commission
  - Tulare County GIS database
  - GAMA & upcoming UCD domestic well surveys
  - USGS NAWQA studies

Other source indicators include other groundwater age & vulnerability, other isotopic systems (C, B), chemistry (major anion ratios, Br, I), and co-contaminants (agrichemicals, pharmaceuticals, xenobiotics).

Nitrate source attribution in Tulare County domestic wells:
The isotopic evidence is indicative of multiple anthropogenic sources

- **Nitrate isotopic data on a subset of Tulare County domestic wells does not definitively constrain the nitrate source to these wells**
  - The observed pattern could be produced by a single source (natural soil N) or by mixing between multiple sources (fertilizer, manure, septic).
- **The isotopic composition of water in domestic wells constrains the source of recharge as local precipitation in the foothills, and irrigation in the valley**
  - Foothill wells are recharged by local precipitation, and have low nitrate.
  - Valley wells are recharged by irrigation water (from Kings or Kaweah Rivers), and have moderate to high nitrate.
- **Nitrate isotopic composition appears to vary with land use**
  - Dairy, agricultural/residential, and wild-land sites are isotopically distinct
  - Dairy site nitrate-N data are isotopically consistent with a manure source
  - Nitrate-O data are isotopically consistent with local nitrification of ammonium (from either manure, septic, or fertilizer)
- **The isotopic evidence is consistent with the multiple source hypothesis**
  - High concentrations of nitrate occur in all developed land use categories.
  - Domestic wells located close to dairies do have a different nitrate isotopic composition than wells not close to dairies in similar hydrogeologic settings.
  - The isotopic compositions measured are consistent with the suspected sources of nitrate to these wells (soil, fertilizer, manure, septic or community wastewater).

Sparse data set under-represented in low-nitrate well waters, and simple approach to assigning land use limit conclusions, but patterns observed are suggestive of multiple anthropogenic sources.